SYNTHETIC ASPECTS OF COMPLEXES OF GROUP 6 ELEMENTS WITH

TRITHIAZYLTRICHLORIDE AND α,α'–DIIMINES, THEIR REACTIVITY, SOLVATOCHROMIC, ESR AND OTHER RELATED STUDIES

A Thesis Submitted
in Partial Fulfilment of the Requirements
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DOCTOR OF PHILOSOPHY

by
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to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

OCTOBER, 1988

To my parents
with regards

CHM—1988—D—SET—SYN

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor U.C. Agarwala.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Jyoti Seth

Kanpur:
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CERTIFICATE OF COURSE WORK

This is to certify that Ms. Jyoti Seth has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

Chm 505	Principles of Organic Chemistry
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Chm 525	Principles of Physical Chemistry
Chm 541	Advanced Inorganic Chemistry I
Chm 542	Advanced Inorganic Chemistry II
Chm 545	Principles of Inorganic Chemistry
Chm 800	General Seminar
Chm 801	Special Seminar
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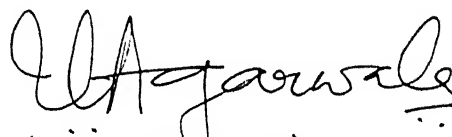
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Certified that the work contained in this thesis entitled: ''SYNTHETIC ASPECTS OF COMPLEXES OF GROUP 6 ELEMENTS WITH TRI-THIAZYLTRICHLORIDE AND α,α'-DIIMINES, THEIR REACTIVITY, SOLVATO-CHROMIC, ESR AND OTHER RELATED STUDIES'', has been carried out by Ms. Jyoti Seth, under my supervision, and the same has not been submitted elsewhere for a degree.

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PREFACE

Recognition of photoinduced redox properties of tris(2,2'-bipyridine)ruthenium(II) $Ru(bipy)_3^{2+}$, has spurred numerous studies on the complex and its related derivatives. Their optical excitations have led to population of a luminescent metal to ligand charge transfer (MLCT) state, which can act as an oxidizing or reducing agent. Current interest centers on minimizing the reverse reaction that follows photoinduced electron transfer and converting the one photon, one electron redox step into more useful multielectron transfer reactions. Semiconductors, electron relay reagents and catalysts are being investigated as a means of storing electrons and imitating multielectron reactions. Another approach is the use of di or polymeric complexes which could in principle act as a two/multielectron transfer reagents when excited by photons. However, in such complexes, certain life time constraints are to be satisfied. Although a number of low spin d^6 metal complexes have previously been prepared for the purpose of studying the intervalence charge transfer (IT) transition in the mixed valence systems, very few satisfy the criteria of field strength and/or coordination about each metal ion necessary for luminescence which is not necessarily a prerequisite for photo redox behavior, its presence is however, desireable because of its being a convenient probe of the excited state and its redox potentials. It will therefore, be interesting to work on di/polynuclear complexes of

d^6 systems. In the thesis Group 6 carbonyl metal complexes having α,α'-diimine as bridging ligands have been synthesized and their properties have been studied which may help in the study of photo-induced redox properties of complexes.

Another thrust area of the present research is the synthetic study of metal complex with S-N heterocycles as ligands which may provide information about unstable sulfur-nitrogen intermediates like S_2N_2, $N_3S_2^{3-}$, $NSCl^{2-}$ etc. The studies of these intermediates can further be correlated in terms of the existing bonding theories. An initial step in this direction also forms a part of the thesis.

The subject matter of the first chapter reflects the scope and the objective of the work embodied in the thesis. A brief overview of the chemistry of sulfur-nitrogen compounds containing synthetic strategies of the various coordinating sulfur-nitrogen species and their modes of bonding to the metal center is given. This is followed by a very short account of the polymetallic systems and their important features. A few of the d^6 polymetallic complexes having bidentate aromatic nitrogen heterocycle as the bridging ligand have also been surveyed.

Chapter II describes the reactions of $M(CO)_6$ (M = Cr, W) with the ligands, p-phenylene bis(picolinealdimine) [PBP] and p-biphenylene bis(picolinaldimine) [BBP] whereby the complexes of the type $[M(CO)_4]_2-\mu-$PBP/BBP are formed. Their reactions with the π- acid ligands L' [L' = PPh_3, $AsPh_3$, $SbPh_3$, Py, Diphos] have

been carried out yielding $[M(CO)_3L']_2-\mu-PBP/BBP$ $[M = Mo, W]$. Solvatochromism in the ν_{CO} and the electronic absorption and emission spectral bands has been dealt in detail. The shifts in the solvatochromic MLCT transition bands have been correlated with the various solvent parameters. The energy of the MLCT transition has also been correlated with the electrochemical properties of the system. The chapter also describes some interesting observations made in the chemical reduction of $[Mo(CO)_4]_2-\mu-PBP/BBP$ with Zn-Hg amalgam.

Chapter III describes the reactivity of trithiazyltrichloride towards $[M(CO)_4(L-L)]$ $[M = Cr, Mo, W; L-L = bipy, o-phen]$ where $[CrCl_3(L-L)]_2-\mu-S_2N_2$ and $[M(NSCl)Cl_3(L-L)]$ $[M = Mo, W]$ were obtained. The compounds were characterized by physicochemical methods and the magnetic properties of the paramagnetic complexes studied. From the characteristic electronic spectra of the Cr(III) complexes, ligand field parameters Δ, β_{35} and β_{55} were evaluated.

As a result of the reactions of the complexes $[M(CO)_3X_2(L-L)]$ $[M = Mo, W; X_2 = Br_2, I_2; L-L = bipy, o-phen]$ with trithiazyltrichloride, the chlorothionitrene complexes of the metal in +6 oxidation state were prepared. The coordinating mode of the NSCl in the complexes were speculated by thermolysis reactions and by the reactions of the diimines with the known thionitrene complexes of molybdenum and tungsten. This forms the subject matter of chapter IV.

Chapter V deals with a few cyclothiazeno pyridine and diimine complexes synthesized from $[Mo(N_3S_2)Cl_3]_2$ and $[Mo(N_3S_2)-Cl_3]_2-\mu-S_2N_2$ in varying yields. An effprt has been made to account for the enhanced yield of the products when $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$ is used as a precursor. The compounds exhibited interesting ESR spectra showing axial distortion. The analyses of the molecular zeeman tensors (g and A) were carried out by fitting computer simulated line shape. Using g value shifts and the electronic transitional energies obtained from their electronic spectra, the information about the spin-orbit mixing and the molecular orbital coefficients for the metal ligand bonding were calculated. From these results the importance of σ - and π - contributions in the metal-nitrogen bonding involving metal 4d, $N_3S_2^{3-}$ and diimine/pyridine orbitals have been highlighted.

Chapter VI describes the oxidation of arene tricarbonyl molybdenum(O) with trithiazyltrichloride and the effect of the substituent groups on the arene ring on the rate of reaction. A qualitative comparison of the oxidizing behavior of trithiazyl trichloride is made with other oxidizing agents.

The last chapter gives in brief the summary of the work presented in the thesis along with a few suggestions and recommendations for future work.

CONTENTS

CHAPTER-I

INTRODUCTION

I.1   Scope and Objective

The advances in the chemistry of the most diverse and probably the most studied complexes of d^6 transition metal ions have appeared to dominate the progress in recent years. Their contributions in undergoing a variety of photoreactions and energy transfer processes[1] and in forming mixed valence polymetallic systems[2] partially reflect the growth in this area. Some of the facets of their exceedingly interesting behavior are dominated by the π-basic properties of the metal ions. Being rich in π-d electron density, the charge can be delocalized over the vacant π^* orbitals of the ligand thus imparting a pronounced effect on the redox properties of the complexes.

One among the various other important properties of d^6 complexes is their application as catalysts.[3] These have been used in processes like alkene hydrogenation, reduction of aldehydes

and ketones to alcohols, dimerization of ethylene. Group 6 arene carbonyls have also been used for the understanding of the reaction mechanism in organic chemistry.

Most reaction mechanism studies have been focused on low spin d^6 systems which are thermally photosubstitution unreactive, thereby simplifying the characterizations of reactants and products. Ligand substitution represents the most common unimolecular chemical reaction by which electronically excited metal complexes undergo deactivation. The photosubstitution behavior of ligand L (L = aromatic nitrogen heterocycle) in the complexes like $[Ru(NH_3)_5L]^{2+}$[4,5], $[Fe(CN)_5L]^{3-}$[6], $[W(CO)_5L]$[7] is dependent upon their lowest lying excited state. For complexes in which the lowest triplet ligand field (^{3}LF) excited state is lower in energy than the MLCT, initially populated manifold, the photosubstitution reactions which occur upon irradiation are efficient. However, when the MLCT excited state is tuned to an energy lower than the ^{3}LF excited state by changing the nature of L, a dramatic decrease in the photosubstitution results.

Rh(III)[8], Ru(II)[9] complexes have been used for the photoreduction of water to H_2. The photoreduction of H_2O to H_2 can occur with visible light by irradiation of $Ru(bipy)_3^{2+}/Ru(bipy)_3^{3+}/$Triethanolamine/$H_2O$/Pt systems. In a similar way $Rh(bipy)_3^{3+}$ complex can also be used. It also has suitable redox potential.

Despite the large amount of work on the interesting photo-physical properties of the d^6 complexes, very little attention has been paid to the zerovalent organometallic complexes. Thus group 6 carbonyls have the potential of forming mononuclear and binuclear systems having diimine as ligands L. Cr, Mo and W carbonyl fragments bound to nitrogen-aromatic bridging ligand have also received some attention in the literature as antenna fragments in the formation of polymetallic complexes. An advantage of the metal carbonyl antenna fragments is the negative solvatochromism of their MLCT transition in a wide variety of solvents. The energy of the MLCT state of the antenna fragment could potentially be tuned to probe or exploit the acceptor levels of the reactive fragment with the use of differential solvents only.

It is evident from the properties of d^6 transition metal complexes described in the preceeding paragraphs that a large number of their very interesting properties can be studied and explored. We have synthesized a few bimetallic systems having α,α'-diimine as the bridging ligand and studied their solvato-chromism in detail. The interesting aspect of these reactions was the photoinertness of the ligand, highly absorbing MLCT transitions and emission in solution. These properties are also pre-requisite to study the bimolecular photocatalyzed water splitting and energy transfer processes.

Another interesting area which has attracted the attention
of both theoreticians and experimental chemists is the chemistry
of sulfur-nitrogen compounds. Though the complexes of transition
metal ions with sulfur-nitrogen ligands were described in the early
part of the century,[10-12] they still warrant attention because of
the useful information they provide about the unstable inter-
mediates like NS^+, S_2N_2, $N_3S_2^{3-}$, $NSCl^{2-}$ etc. These species can be
stabilized through their coordination with the metal ions. Since
the discovery of unusual conducting properties of $(SN)_x$ there has
been continuous sustained interest in this area. These species
have the potential of forming 1-dimensional materials with interest-
ing anisotropic properties. Though many workers have reported
infra red spectral and crystallographic structures of a number of
metal complexes containing these electron rich sulfur-nitrogen
rings and cages as coligands, no report aimed at understanding the
nature of bonding in these complexes has appeared in the literature.
The latter studies warrant attention, in particular, for the possi-
ble solution of the problem as to why metal complexation stabilize
these species. It is surprising that their electronic spectra and
magnetic properties have not been studied. The reason for the lack
of such a study could be due to the fact that a large number of
reported complexes are diamagnetic which could not be explored
using the technique such as ESR.

Another difficulty associated with the chemistry of sulfur-
nitrogen compounds is the lack of a suitable thionitrosylating

reagent. From the literature known synthetic procedures it appears that the reactivity of the reagent depends on the reaction conditions, nature of the metal ion, etc. Among the various such reagents, trithiazyltrichloride seems to be one of the most versatile reagent for the synthesis of these complexes. However, its behavior is also unpredictable. In this work, all attempt has therefore been made to study the reactivity of trithiazyltrichloride on the group 6 metal complexes. The paramagnetic complexes of the metals in +5 oxidation state (d' system) are characterized by their magnetic properties and ESR spectra which are particularly amenable to analysis. Results of these studies indicate the importance of σ and π contributions in the metal nitrogen bonds, thereby enabling the study of bonding of nitrogen-sulfur species to the metal center.

With the aims in view, we have carried out the following:

(i) <u>Synthesis, characterization and solvatochromic properties of Group 6 metal carbonyls having Schiff base of pyridine carbaldehyde as bridging ligand</u>

New binuclear complexes $[M(CO)_4]_2L$ (M = Cr, W; L = p-phenylene bis(picolinaldimine) [PBP] or p-biphenylene bis(picolinaldimine) [BBP] are synthesized and their reactions were carried out with various π-acceptor ligands. The influence of the π-acceptor properties of the ligands in relation to their stabilities, studied. Their spectroscopic and electrochemical properties have been studied and a detailed account of solvatochromic behavior of the

MLCT transition is discussed. The results of oxidative addition reactions of $[M(CO)_4]_2$PBP/BBP (M = Mo,W) with iodine and mercuric chloride have also been described. The results form the contents of chapter II.

(ii) Reactivity of Trithiazyltrichloride towards $[M(CO)_4(L-L)]$ (M = Cr, Mo, W; L-L = bipy, o-phen)

The reactions of the trithiazyltrichloride with $[M(CO)_4(L-L)]$ (M = Mo, W; L-L = bipy, o-phen) were carried out in dichloromethane whereby the compounds of the type $[CrCl_3(L-L)]-\mu-S_2N_2$ and $[M(NSCl)-Cl_3(L-L)]$ (M = Mo, W) were obtained. The compounds were characterized by the physicochemical methods. The bonding nature of the ligands has also been discussed. The results of these are embodied in chapter III of the thesis.

(iii) Chlorothionitrene complexes of Molybdenum(VI) and Tungsten(VI)

Synthesis of chlorothionitrene complexes of Mo(VI) and W(VI) by the reactions of M(II) carbonyl complexes (M = Mo, W) with trithiazyltrichloride has been described in chapter IV. The compounds were characterized by various physical and chemical studies.

(iv) Synthetic and bonding aspects of cyclothiazeno complexes of Molybdenum(V)

The reactions of $[Mo(N_3S_2)Cl_3]_2$ and $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$

with py, bipy or o-phen yielded cyclothiazeno complexes having py, bipy or o-phen as coligands in 20% and 80% yield respectively. The spin Hamiltonian parameters were extracted from their ESR spectra in polycrystalline samples and in solution (CH_2Cl_2) recorded at 298K and from those of the magnetically dilute glass /polycrystalline sample taken at 77K. These parameters and the data obtained from the electronic spectra were used to calculate the molecular orbital coefficients. A plausible mechanism is also suggested. These results have been described in chapter V.

(v) Reactivity of Trithiazyltrichloride towards arene tricarbonyl molybdenum(O) complexes

Oxidation of arene tricarbonyl molybdenum(O) with trithiazyltrichloride has been studied at room as well as at low temperature ($-78^{O}C$). The effect of substituent group on the benzene ring in relation to the rate of reaction was studied and a comparison of the reaction rate was made with other oxidizing agents. The preliminary results of these reactions have been given in chapter VI of the thesis.

Considering the fascinating aspects of the syntheses and versatility of the sulfur nitrogen ligands, it will be appropriate to have a brief overview of the work done so far with these molecules. This has been described in the following part of the introduction. The latter part of the introduction gives a short account of the bimetallic systems, and their important properties.

I.2   Complexes of Inorganic Sulfur-nitrogen ligands

Though to a casual observer, the methods used for the preparation of S-N heterocycles are often obscure and even the expert will be having some difficulty in predicting the nature of such reactions. The S-N heterocycles can in general be prepared by treating S_4N_4, $S_3N_2Cl_2$ or $(NSCl)_3$ with various reagents. S_4N_4 and cyclothiazyl halides can be synthesized conveniently from ammonia or ammonium halides and sulfur halides. The other routes for the syntheses of S-N heterocycles include Si-N or Sn-N reagents, metallocyclothiazenes, S-N cations, anions and oxides. An excellent review has already appeared in the literature covering the synthesis, properties and the nature of bonding in S-N compounds.[13] Since our interest in the thesis lies in synthesizing the complexes formed by the sulfur-nitrogen compounds, the following is a very brief overview of the advances made related to their chemistries in the recent years.

I.2a   Complexes of Sulfur-nitrides

(i)   Thionitrosyl complexes 'NS'

Despite a wide development of nitrosyl chemistry, it is only in recent years that compounds containing thionitrosyl ligand have been prepared. The first thionitrosyl complexes of Mo, Re and Os were first reported in the literature by Chatt and coworkers in 1974 from the reactions of their nitrido complexes with sulfur.[14-16]

$$MoN(S_2CNR_2)_3 + S_8 \longrightarrow Mo(NS)(S_2CNR_2)_3 \qquad \text{.. (1)}$$

$$R_2 = 2Me, \ 2Et \ or \ (CH_2)_5$$
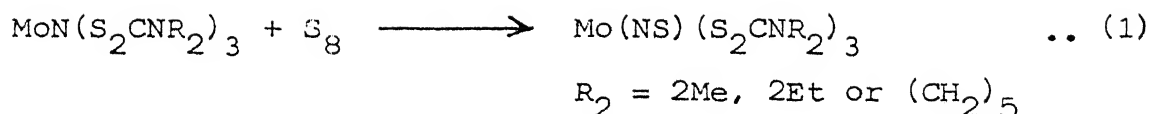
The same preparatory route has recently been extended to Tc(I) and Tc(II) complexes[17]

$$L_3TcCl_2N + S_2Cl_2 \longrightarrow L_3TcCl_x(NS) \qquad \text{.. (2)}$$

$$L = PhMe_2P, \ x = 2 \ or \ 3$$
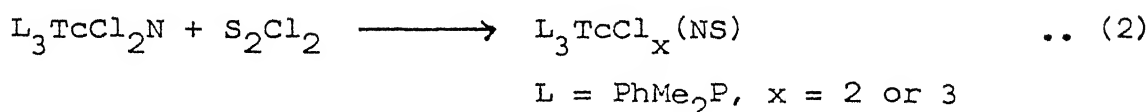
The use of NS^+ salt with $PF_6{}^-$[18], $AsF_6{}^-$[19] etc has the potential to become a general method of synthesis but the approach has been exploited only for a few reactions.

$$(C_6H_6)Cr(CO)_3 + [NS][PF_6] \xrightarrow{MeCN} [Cr(NS)(MeCN)_5][PF_6]_2 \quad \text{.. (3)}$$

$$[CpFe(CO)_2SO_2][AsF_6] + [NS][AsF_6] \longrightarrow [CpFe(CO)_2NS][AsF_6]_2 + SO_2$$

$$\text{.. (4)}$$
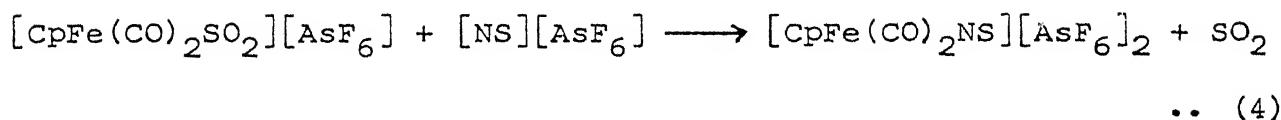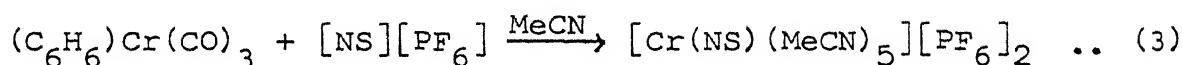
Use of $(NSCl)_3$, trithiazyltrichloride as a source of NS^+ was first reported in 1978 by Kolthammer and Legzdins[20] for the organometallic thionitrosyl complexes

$$Na[CpCr(CO)_3] + (NSCl)_3 \longrightarrow CpCr(CO)_2NS + CO + NaCl \qquad \text{.. (5)}$$
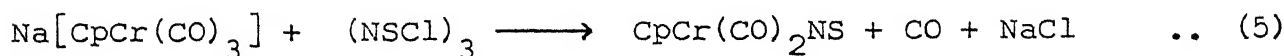
During the same period, the use of $(NSCl)_3$ has also been explored by Agarwala and coworkers for the synthesis of thionitrosyl complexes of Ru, Os, Co etc.[21-24]

$$[RuCl_3(PPh_3)_2] + (NSCl)_3 \xrightarrow{THF} [Ru(NS)Cl_3(PPh_3)_2] \qquad .. \quad (6)$$

$$[CoH\{P(OPh_3)\}_4] + (NSCl)_3 \xrightarrow{THF} [Co(NS)Cl_2\{P(OPh_3)\}_2] \longrightarrow$$

$$[Co(NSO)Cl_2\{P(OPh_3)\}_2] \qquad .. \quad (7)$$
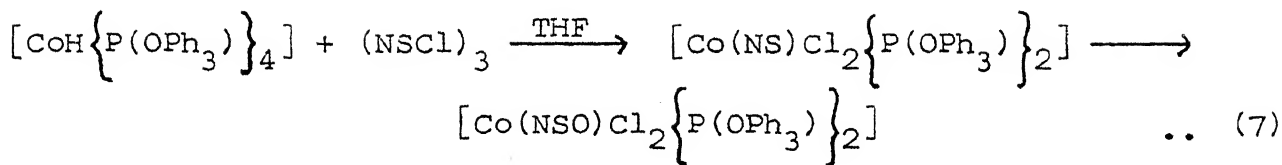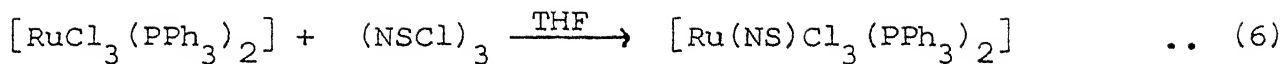
Recently, the use of S_4N_4 has also been reported in the synthesis of NS complexes[25]

$$Re_2Cl_{10} + S_4N_4 \xrightarrow[CH_2Cl_2]{PPh_4Cl} [PPh_4][Re(NS)Cl_5] \qquad .. \quad (8)$$
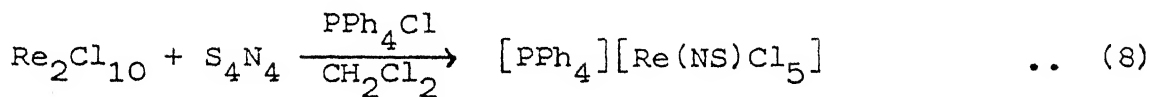
Although a number of thionitrosyl complexes have been reported, only a few ones have been characterized by X-ray crystallography. In all the complexes M—N S unit is essentially linear and unlike metal nitrosyls there are no confirmed examples of either bridging or bent thionitrosyl ligand. The $\nu_{NS}+$ band in the thionitrosyl complexes fall in the broad range of 1065-1390 cm^{-1}. Other studies like ^{13}C and ^{14}N NMR have been carried out on these complexes[26] and the results are compared with the nitrosyl analogues.

(ii) Complexes of disulfurdinitride (S_2N_2)

Due to the difficulties in synthesizing free S_2N_2 and its low stability, the complexes of S_2N_2 have not been obtained by the reactions of S_2N_2 and the metallic salts/complexes. Instead, coordinated S_2N_2 has been used as a source of S_2N_2 for their preparations. The most commonly used S_2N_2 source is its complex

formed with strong Lewis acid like S_2N_2, $2BCl_3$. The latter is obtained from the reaction of S_2N_2 dissolved in methylene chloride with an excess of BCl_3 at $-78^\circ C$.[27] The other complexes are usually prepared as

$$RuCl_2(CO)_2(PPh_3)_2 + S_2N_2 \cdot 2AlCl_3 \xrightarrow{CH_2Cl_2} [RuCl(S_2N_2)(CO)_2(PPh_3)_2]^+-$$
$$AlCl_4^- + AlCl_3 \qquad .. \ (9)$$
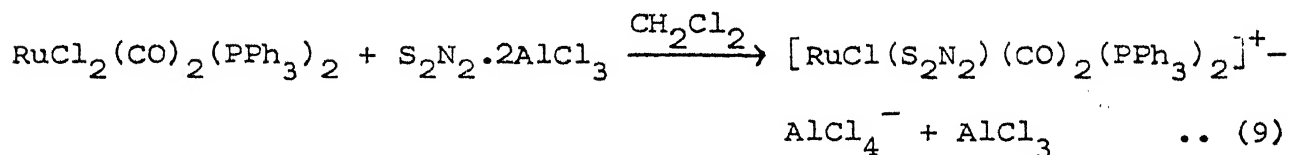
Several cases are known in which the reaction of S_4N_4 with a Lewis acid directly yields an S_2N_2 complex with the Lewis acid. Their reaction kinetics is not known, though it is assumed that initially a donor-acceptor complex between S_4N_4 and the Lewis acid is formed which on thermolysis gives the required S_2N_2 complex.[28]

$$2S_4N_4 \cdot TiCl_4 \longrightarrow 2S_2N_2 \cdot TiCl_4 + S_4N_4 \qquad .. \ (10)$$
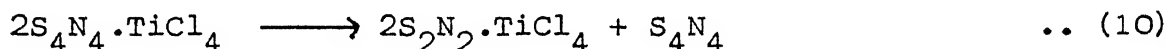
These complexes can also be formed by the direct action of S_4N_4.[29]

$$2MoBr_4 + 2S_4N_4 \longrightarrow [MoBr_3(N_3S_2)]_2-\mu-S_2N_2 + S_2Br_2 \qquad .. \ (11)$$

$$2M(CO)_6 + 2S_4N_4 + 4Br_2 \longrightarrow [MBr_3(N_3S_2)]_2-\mu-S_2N_2 + S_2Br_2 + 12CO$$
$$M = Mo, W \qquad .. \ (12)$$
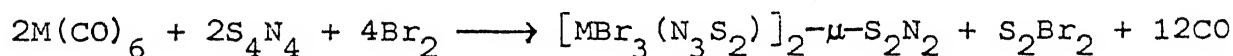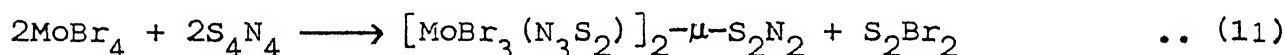
$(NSCl)_3$, trithiazyltrichloride has also been used for the syntheses of S_2N_2 complexes. The interaction with a metal halide possessing Lewis acid properties can occur between the nitrogen atom of the monomer, NSCl or nitrogen atom of the trimer $(NSCl)_3$, followed by ring cleavage. In either case, formation of a donor-acceptor

complex between the metal halide and a NSCl molecule results[30,31] which immediately yields S_2N_2 complex by a secondary reaction.

$$2MCl_5 + 2NSCl \longrightarrow 2[Cl_5-M-N\equiv S_{\ Cl}] \longrightarrow [Cl_5-M-S_2N_2-MCl_5] + Cl_2$$
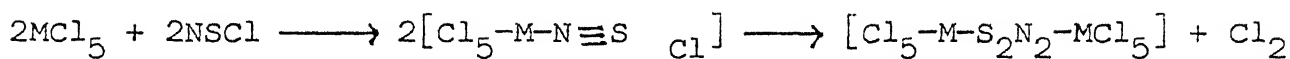
M = Nb, Ta .. (13)

depending upon the reaction conditions and the metal involved. The same reaction leads to different types of products under different reaction conditions. Polar solvents influence the reaction paths of the metal halides with trithiazyltrichloride. The nature of soluble donor-acceptor complex formed during the reactions also seem to play a dominant role.

$$2CuCl + (NSCl)_3 + 2MeCN \longrightarrow N_2S_2.2CuCl-2MeCN \xrightarrow{\Delta} N_2S_2.2CuCl$$

.. (14)

$$MoCl_5 + (NSCl)_3 \longrightarrow S_2N_2[MoCl_4(NSCl)]_2 + 2SCl_2 ^{52}$$ .. (15)
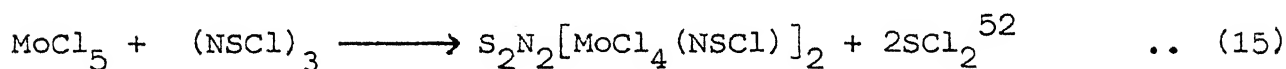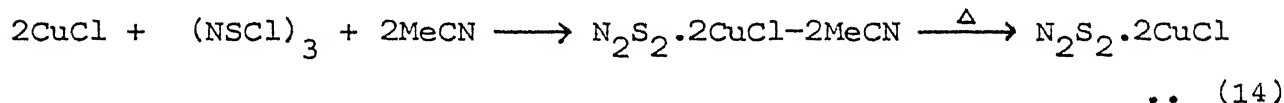
Trithiazyltrichloride reacts with powdered chromium, chromium oxide and other group 6 metal carbonyls to yield S_2N_2 and other (S-N) ligand complexes, depending upon the reaction conditions.[29,33] Thus,

$$Cr + 2(NSCl)_3 \longrightarrow S_4N_3^+[S_2N_2.CrCl_4]^- + \frac{1}{2}N_2 + Cl_2$$ .. (16)

$$M(CO)_6 + (NSCl)_3 \longrightarrow [MCl_3(N_3S_2)]_2 + S_2Cl_2 + 12\ CO$$ .. (17)
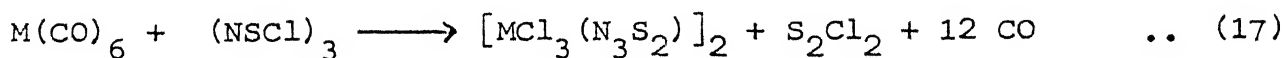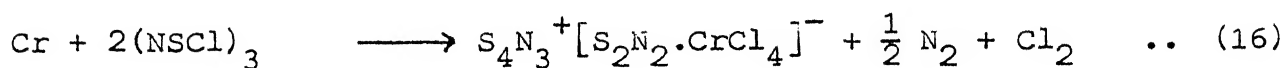
M = Mo, W

Trithiazyltrichloride reacts with nitrides to give S_2N_2 complexes.[34]

$$[\text{ReNCl}_3 \cdot \text{POCl}_3]_4 \cdot 2\text{POCl}_3 \longrightarrow [\text{ReCl}_3(\text{NSCl})]_2 \cdot \text{S}_2\text{N}_2 + 2\text{N}_2$$

$$+ \, 2\text{Cl}_2 + 3\text{POCl}_3 \qquad \qquad \cdots \,(18)$$
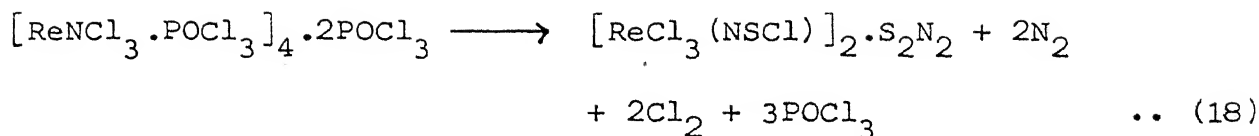
Although S_2N_2 cannot be obtained by the pyrolysis of S(NSO)_2, the elimination of SO_2 from this precursor in the presence of TiCl_4 gives $\text{TiCl}_4 \cdot \text{S}_2\text{N}_2$ in 95% yield.[35]

$$\text{S(NSO)}_2 + \text{TiCl}_4 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{TiCl}_4 \cdot \text{S}_2\text{N}_2 + \text{SO}_2 \qquad \cdots \,(19)$$
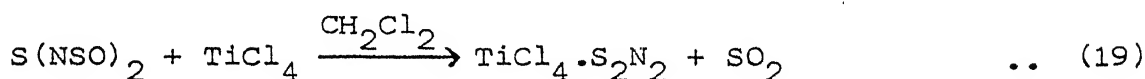
In almost all the well characterized S_2N_2 complexes, S_2N_2 is bidentate bridging ligand with nitrogen atoms as donor site. The geometry of the coordinated S_2N_2 molecule is not substantially different from that of the square planar free ligand. The one exception where S_2N_2 is monodentate is $[(\text{PPh}_3)_2(\text{CO})_2(\text{S}_2\text{N}_2)\text{RuCl}]-[\text{AsCl}_4]$. By complexation of both the nitrogen atoms, the local D_{4h} symmetry is preserved exactly or to a good approximation and the selection rule remains same as for the free ligand. The out of plane deformation essentially is uninfluenced by complexation and is always observed as a sharp and intense band at 470 cm^{-1}. The B_{3u} mode, however is shifted from 795 cm^{-1} to 860 cm^{-1}. Owing to the high intensity and characteristic wave number, the 860 cm^{-1} band is ideally suited for the identification of S_2N_2 ring in the complex. A detailed account of other spectroscopic measurements are presented in a review by Dehnicke and Muller.[36]

(iii) Complexes of Tetrasulfur tetranitride (S_4N_4)

A number of adducts of S_4N_4 with transition metal halides like $MoCl_5 \cdot S_4N_4$[37], $TiCl_4 \cdot S_4N_4$[38] etc. have been reported in the early literature. These can be synthesized by the direct treatment of S_4N_4 with metal halides.[39-41] In addition to the adduct formation, these reactions lead to the fragmentation of S_4N_4 to give S_2N_2 complexes or redox reaction with the formation of S-N cations or cyclometallathiazenes.

$$CuCl_2 + S_4N_4 \xrightarrow{CH_2Cl_2, \ CCl_4} CuCl_2 \cdot S_4N_4 \text{[41]} \qquad \ldots (20)$$

$$VCl_2 + S_4N_4 \longrightarrow VCl_4S_2N_2 + \left[VCl_2(N_3S_2)\right]_n \text{[42]} ..(21)$$
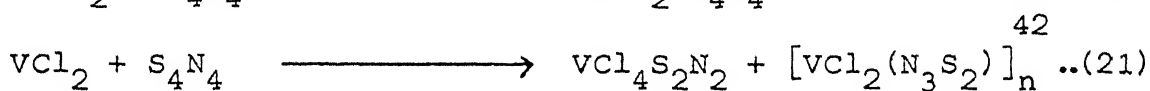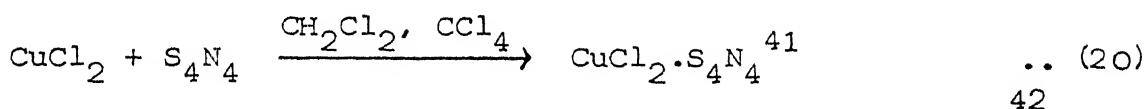
In all the adducts characterized so far by X-ray crystallography, S_4N_4 is coordinated to the metal via one of the nitrogen atoms. The structural consequence of this coordination is the disruption of cross S-S bonds of S_4N_4 to give the boat shaped eight membered ring with approximately coplanar sulfur atoms and similar S-N bond distances. Another coordination mode exhibited by S_4N_4 is where metal is bridged via 1,3 bidentate S_4N_4 ligands, e.g. in $CuCl_2 \cdot S_4N_4$.

I.3b Complexes of Thiazyl Halides

(i) Thiazyl Fluoride

The chemistry of NSF has been surveyed by Glemser and Mews.[43] The bent NSF molecule[44] can be easily synthesized by the decomposition of $FC(O)NSF_2$ or $Hg(NSF)_2$[43] but its moisture sensitivity and

thermal instability makes it difficult to handle. Its complexes can however be prepared in liquid sulfur dioxide.[45]

$$[M(SO_2)_2][AsF_6]_2 + 6NSF \longrightarrow [M(NSF)_6][AsF_6] + 2SO_2 \quad .. \quad (22)$$

$$[Re(CO)_5SO_2][AsF_6] + NSF \xrightarrow[SO_2]{-30^oC} [Re(CO)_5NSF][AsF_6] + SO_2 ..(23)$$
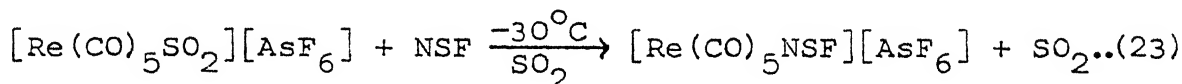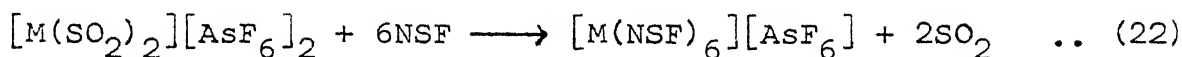
(ii) Thiazyl chloride

The first transition metal complexes of NSCl was discovered in 1982[47] and within a few years these compounds have become a well established group of S-N complexes. Trimeric $(NSCl)_3$ has proved to be a convenient route for the preparation of M-NSCl complexes. However the reactions give rise to other complexes also having different S-N heterocycles as ligands.

$$MCl_5 + (NSCl)_3 \longrightarrow MCl_5(NSCl)^{[48,49]} \qquad .. (24)$$

M = Nb, Ta

$$VCl_4 + (NSCl)_3 \longrightarrow [VCl_3(NSCl)]_2^{[50]} \qquad .. (25)$$

$$ReCl_5 + (NSCl)_3 \xrightarrow{POCl_3} [ReCl_4(NSCl)(POCl_3)] +$$

$$[ReCl_3(NSCl)_2(POCl_3)]^{[47,51]} \qquad .. (26)$$

$$Mo_2Cl_{10} \text{ or } WCl_5 + (NSCl)_3 \xrightarrow{CH_2Cl_2} [MCl_4(NSCl)]_2 \xrightarrow{POCl_3}$$

$$[MCl_4(NSCl)(POCl_3)]^{[52,53]} \qquad .. (27)$$

$$MoCl_5 \text{ or } WCl_6 + (NSCl)_3 \longrightarrow [M(NSCl)_4]_2 \text{-}\mu\text{-}S_2N_2^{[53]} \qquad .. (28)$$

$$Mo_2Cl_{10} \text{ or } MoCl_4 + (NSCl)_3 \longrightarrow [N(SCl)_2][Mo(NSCl)Cl_5]^{54} \quad ..(29)$$

$$OsCl_5 + (NSCl)_3 \longrightarrow [OsCl_4(NSCl)]^{55} \quad ..(30)$$
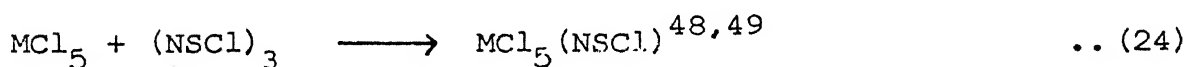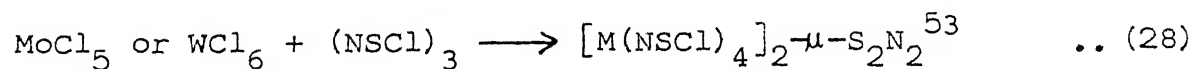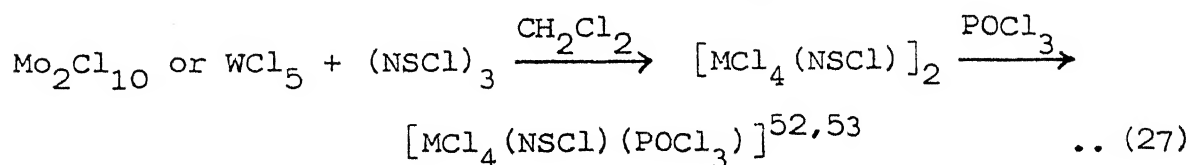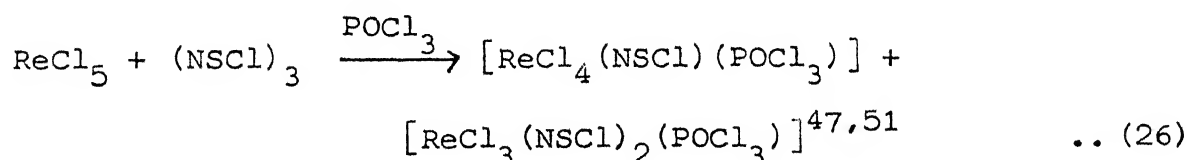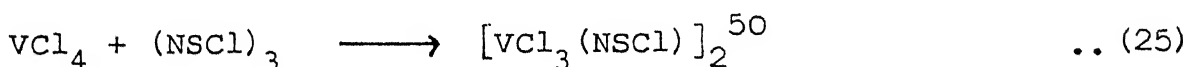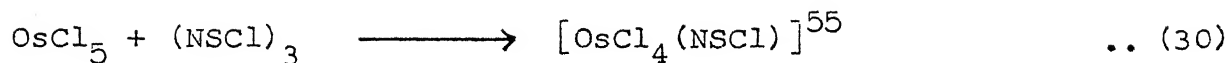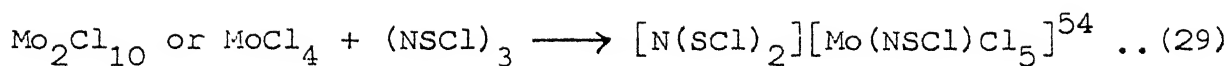
M—NSCl complexes can also be prepared by the use of $S_3N_2Cl_2$ with metal halides

$$WCl_6 + S_3N_2Cl_2 \xrightarrow{CCl_4} [N(SCl)_2][WCl_5(NSCl)]^{32} \quad ..(31)$$

$$ReCl_5 + S_3N_2Cl_2 \xrightarrow[POCl_3]{CH_2Cl_2} [ReCl_3(NSCl)_2]_2 \longrightarrow$$
$$[ReCl_3(NSCl)_2POCl_3]^{56} \quad ..(32)$$
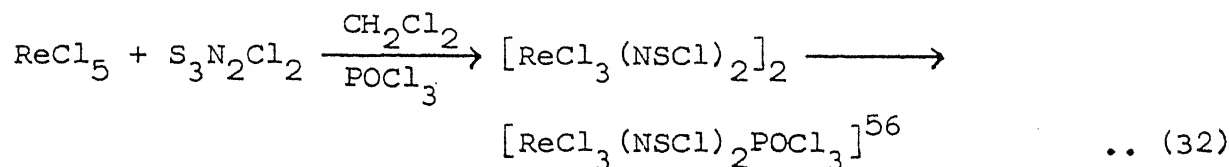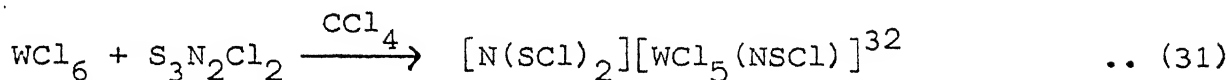
The NSCl complexes can also be prepared by (1) Addition of chloride ion[57] to coordinated NS groups (2) Insertion of NS^+ into metal halogen bond and (3) Halogen exchange of coordinated NSF.

$$[Re(CO)_5NS][AsF_6] + CsX \xrightarrow{SO_2} [Re(CO)_5NSX][AsF_6] + CsAsF_6 \quad ..(33)$$

$$[Re(CO)_5X] + [NS][AsF_6] \xrightarrow{SO_2} [Re(CO)_5NSX][AsF_6] \quad ..(34)$$

$$[Re(CO)_5NSF][AsF_6] + \tfrac{1}{4}SiX_4 \xrightarrow{SO_2} [Re(CO)_5NSF][AsF_6] +$$
$$\tfrac{1}{4}SiF_6 \quad ..(35)$$
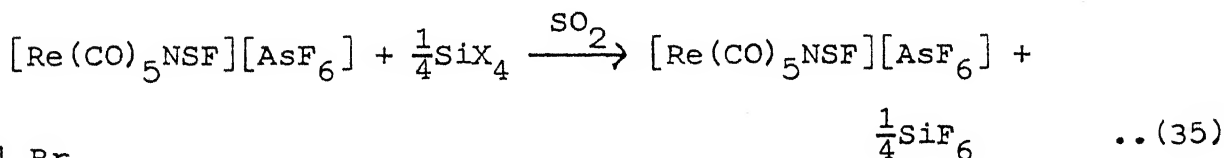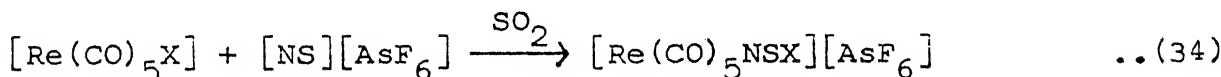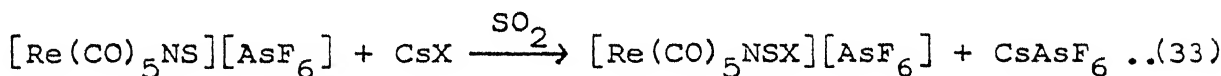
X=Cl,Br

The neutral M—NSCl complexes can be converted into ionic soluble complexes by the treatment of R_4PCl or R_4AsCl (R = Me, Ph)[46,51]

$$[ReCl_3(NSCl)_2(POCl_3)] + AsPh_4Cl \xrightarrow{CH_2Cl_2} \quad ..(36)$$
$$[AsPh_4][ReCl_4(NSCl)_2].CH_2Cl_2$$

$$[MoCl_4(NSCl)POCl_3] + R_4ECl \longrightarrow [R_4E][MoCl_5(NSCl)] \qquad \cdots (37)$$
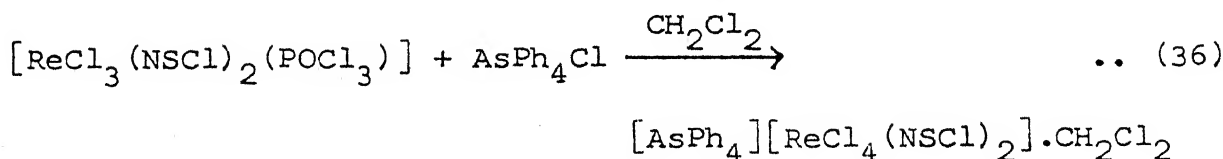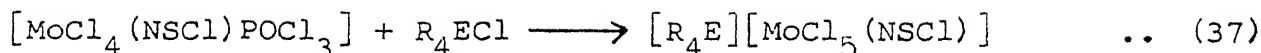
E = P, As

On thermolysis chlorothionitrene complexes (M-NSCl) yield nitrido complexes and provide a new synthetic route for the synthesis of transition metal nitrides.[52]

$$[ReCl_4(NSCl)POCl_3] + AsPh_4Cl \longrightarrow [AsPh_4][ReNCl_4] \qquad \cdots (38)$$

$$[MoCl_4(NSCl)_2] \xrightarrow{\ 130^{\circ}C\ } 2MoNCl_3 + 2SCl_2 \qquad \cdots (39)$$
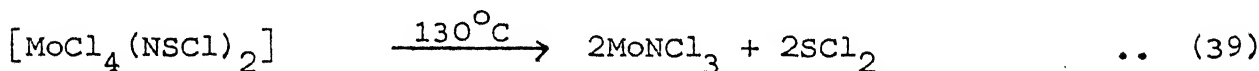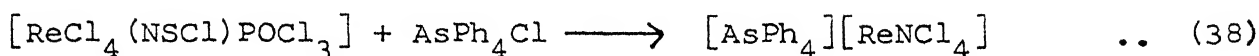
The weakly coordinated NSCl ligand can be substituted by chloride ions.[50]

$$[MCl_5(NSCl)] + AsPh_4Cl \longrightarrow [Ph_4As][MCl_6] \qquad \cdots (40)$$
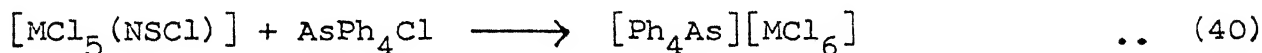
M = Nb, Ta

Reaction of two NSCl ligands with triphenylphosphine result in the coupling of the adjacent thionitrosyl groups with the formation of novel metallathiazene ring.[58]

$$(Cl_3OP)Re\begin{smallmatrix}NSCl\\NSCl\end{smallmatrix} \xrightarrow{\ PPh_3\ } [PPh_3Cl][Cl_4Re\begin{smallmatrix}N-S\\ \ |\\N-S\end{smallmatrix}] \qquad \cdots (41)$$
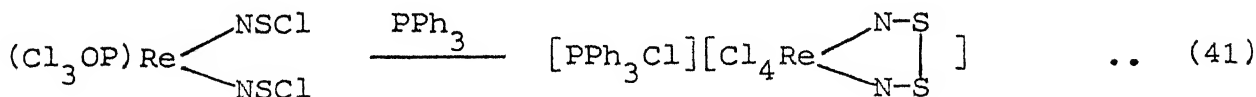
The bonding in metal-NSCl complexes has been described in terms of resonance structures I and II. Spectroscopic and X-ray data indicates the dominance of structure I.

$$M\overset{+}{=}N\overset{-}{=}S\diagdown Cl \qquad\qquad \overset{-}{M}-\overset{+}{N}\equiv S\diagdown Cl$$

I   II
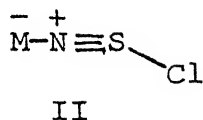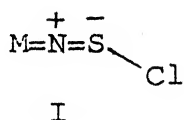
Complexes having the dominance of structure I exhibit a characteristic strong band at 900–1000 cm^{-1} assigned to ν_{as}(MNS), while the one with larger contribution of resonance structure II display a band at 1290–1360 cm^{-1} due to $\nu_{N\equiv S}$.

(iii) Thiazyl Bromide

Unlike trimer (NSCl)$_3$, (NSBr)$_3$ is unknown at present. However monomeric NSBr has been prepared by the pyrolysis of S_4N_3Br in gas phase.[59] NSBr complexes have been prepared by bromide addition to the coordinated NS, by the insertion of NS$^+$ into the metal halogen bond or by the halogen exchange at coordinated NSF. These reactions are similar to the ones already described [Reactions 32–34]. The bromothionitrene complex has also been prepared by treating the thionitrene complex with an excess of trimethylsilylbromide.[60]

$$[WCl_4(NSCl)]_2 + 10\ Me_3SiBr \longrightarrow [WBr_4(NSBr)]_2 + 10Me_3SiCl \quad ..(42)$$
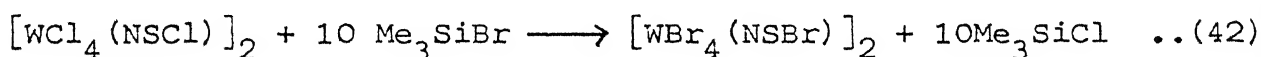
I.2c Cyclometallathiazenes and related complexes

A cyclometallathiazene is defined as a ring system consisting only of sulfur and nitrogen and one or more metal atoms. Cyclometallathiazenes have been formally considered as complexes between cationic metal fragments and binary S–N anions in which both sulfur and nitrogen atoms are two coordinate.[61]

(i) $\underline{MS_2N_2}$

The five membered cyclometallathiazenes MS_2N_2 can be regarded as derivatives of dianion, disulfurdinitride, $S_2N_2{}^{2-}$. Most of the rings of the type L_nM ⟨S–N–N–S⟩ have been synthesized by the reactions of various metal complexes with S_4N_4.

$$PbI_2 + S_4N_4 \xrightarrow{\text{liq.NH}_3} PbS_2N_2(NH_3)\,[62] \xrightarrow[\text{Vacuum}]{80-90^\circ} PbS_2N_2\,[63,64] \quad \text{.. (43)}$$

$$Pb(NO_3)_2 + S_4N_4 \xrightarrow[\text{NH}_3]{\text{CHCl}_3} PbS_2N_2\,[65] \quad \text{.. (44)}$$
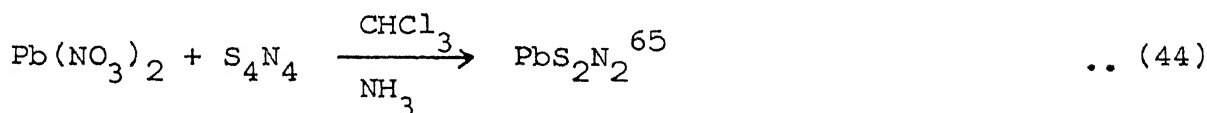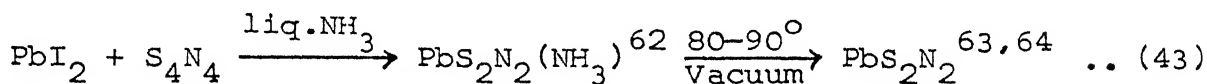
It seems that the formation of mononuclear MS_2N_2 rings from low valent metal complexes involve initial coordination of S_4N_4 to the metal center which promotes cleavage of S_4N_4 to S_2N_2, followed by oxidative addition to the metal. Recently a number of dimeric complexes of S_2N_2 rings have been reported where one of the metal bonded nitrogens of each MS_2N_2 ring is also coordinated to the other metal atom e.g. $[Ph_4P][Ni_3(S_2N_2)_4]\,[66]$.

(ii) $\underline{MS_3N}$

Transition metal complexes containing five membered MS_3N ring are an important and rapidly growing class of cyclometallathiazenes. They differ from other ring systems in the presence of an S–S bond. Recently $[(PPh_3)_2N][S_3N]\,[67,68]$ has been isolated and this reagent provides a convenient route for the syntheses of their complexes.

$$CuCl + [(PPh_3)_2N][S_3N] \longrightarrow [(PPh_3)_2N][CuCl(S_3N)]^{69} \quad \cdots (45)$$

$$AgNO_3 + [(PPh_3)_2N][S_3N] \longrightarrow [(Ph_3P)_2N][Ag(S_3N)_2]^{69} \quad \cdots (46)$$
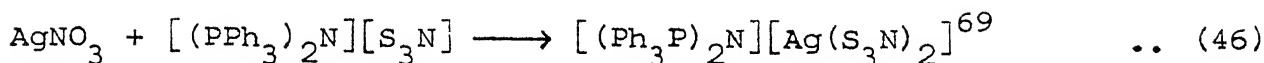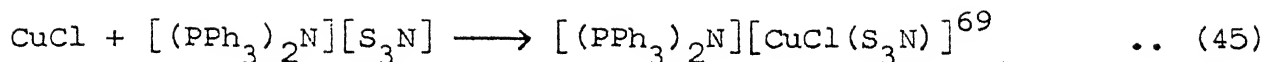
Recently deprotonation of S_7NH with BuLi, followed by trapping of in situ generated S_3N^- ion, by Au in $HAuCl_4$ yielded $[AuCl_2(S_3N)]$.[70]

(iii) $\underline{MS_2N_3}$

The discovery of complexes containing the six membered MS_2N_3 ring is one of the most recent and significant developments in transition metal chemistry of sulfur and nitrogen.

$[Cl_2VS_2N_3]_n$, the first reported MS_2N_3[71] complex has been prepared by the reaction of S_4N_4 with transition metal halides.

$$VCl_4 + S_4N_4 \xrightarrow[\text{Vacuum}]{110^\circ} [Cl_2V(S_2N_3)]_n \quad \cdots (47)$$

$$Mo_2Cl_{10}/WCl_5 + S_4N_4 \xrightarrow{CH_2Cl_2} [Cl_3M(S_2N_3)]_2{}^{72} \quad \cdots (48)$$
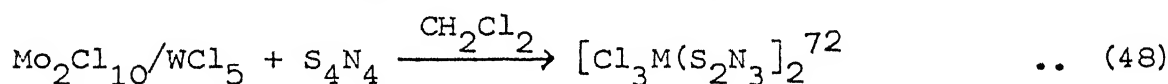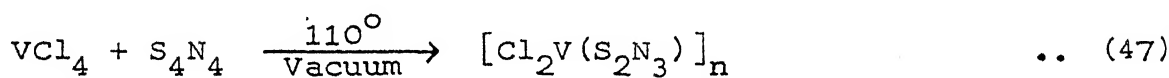
M = Mo, W

The reaction of molybdenum carbonyl with $(NSCl)_3$ was first described by Jolly[73] who formulated it $[MoS_3N_3Cl_3]$. However, the latter studies showed it to be $[Mo(N_3S_2)Cl_3]_2$.[72] With slight variation in the reaction conditions, the same reaction yielded $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$[74]. The tungsten analogue $[W(N_3S_2)Cl_3]_2$[75] has also been prepared by the reaction of $(NSCl)_3$ on $WOCl_4$ or $WSCl_4$.

Transition metal nitrido complexes have also been used in the syntheses of MS_2N_3 rings.[72] $[Mo(N_3S_2)Cl_3]_2$ is obtained by the treatment of $MoNCl_3$ with $(NSCl)_3$ in CCl_4.[75] The cyclization of the complex of the type $[MCl_x(NSCl)]$ by the treatment with $Me_3SiNSNSiMe_3$ potentially represents a controlled synthesis of the MS_2N_3 ring.[72]

The structural data of the $M(S_2N_3)$ groups are compared with those of the related heterocycle $Ph_2PS_2N_3$.[76] The thiazene segment of the ring in the mononuclear complexes is planar like that in $Ph_2PS_2N_3$ while the metal atom is tilted out of plane. The cyclometallathiazenes are regarded as complexes of hypothetical trianion $S_2N_3^{3-}$. The IR spectra of MS_2N_3 complexes show bands between 1000-900 cm^{-1} assignable to ν_{MNS}.[72,75,77]

(iv) $\underline{MS_3N_4}$

The only complex of this eight membered MS_3N_4 ring system in which one of the sulfur atom of S_4N_4 is replaced by transition metal is $[Cp_2TiS_3N_4]$.[78]

(v) $\underline{MS_4N_3}$

The only representative example of MS_4N_3 ring system is $[ClPtS_4N_3]^{[79]}$ which has been prepared from S_4N_4. The MS_4N_3 ring is formally derived from hypothetical anion $S_4N_3^-$ which is

coordinated to the metal atom as bidentate ligand via terminal sulfur atoms and the central nitrogen atom.[80]

(vi) $\underline{MS_2N_4}$

The only example known for this system is the dimer[81]
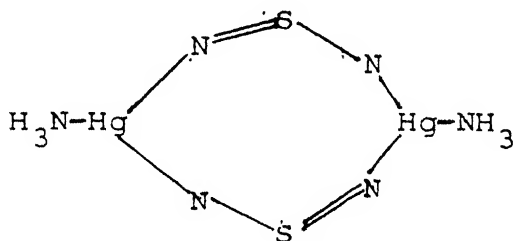
I.3   Bi/Polymetallic Complexes (d^6 System)

Transition metal polymetallic complexes have been of interest as they norish diverse chemical applications such as efficient conductors, surface coatings[82], synthetic models for active site of cytochrome c[83], photocatalyzed processes and electron exchange processes.[84-86] One of the area of recent interest is their use in converting solar radiation to usable chemical potential energy.[87,88] In developing such systems there are many constraints that limit the selection. The desirable system should, in general, have three components: 1) A highly absorbing (antenna) metal center which absorb visible light but is photochemically unreactive; 2) A second metal center which undergoes a useful chemical reaction from a non-spectroscopic excited state; and 3) A bridging ligand which couples the two metal fragments and facilitates intramolecular energy transfer from the antenna to the reactive fragment.

Over the past decade many workers have studied photo-chemical[4,89,90] bimolecular energy transfer[91] and electron transfer reactions[92-94] of Ru(II) complexes of various nitrogen-heterocyclic ligands like substituted pyridines and pyrazine. A variety of pentaammine ruthenium(II) and pentacyanoferrate systems have been explored where the antenna fragments were coupled through monodentate bridging ligand to pentaammine rhodium(III) and penacyano cobaltate(III) reactive fragment.[95] Although the energy transfer reactions were observed in these systems, the major drawback was the thermal and photochemical instability of the metal-ligand-metal bridge. These preliminary studies suggested the use of chelating bridging ligands to maintain the integrity of the complex during the photon absorption/energy transfer/remote reaction sequence.

I.3a Bridging Ligands

Studies on the thermal stability and the electrochemistry of bimetallic complexes illustrate that additional factors, besides the stability of the metal-bridging ligand-metal unit through chelation, need be stressed. In addition to the sites of attachment, another factor in complex stability is the overall charge on the polymetallic unit. In situations where large positive charge is built up, there is a tendency for the complex to decompose to monometallic fragments. Addition of anionic ligands on the metal

center or designed into the bridging ligand reduce the charge on the system.

Most of the bridging ligands forming chelates with metal centers have highly unsaturated aromatic π-systems.

I.3b Antenna Fragments

In developing highly absorbing but photochemically inert metal centers, low valent d^6 complexes of Fe(II), Ru(II), W(O), Mo(O) and Cr(O) were used. These systems were selected because of the thermal stability and intense MLCT transitions associated with complexes of these metal containing aromatic nitrogen heterocyclic ligands. Another interesting feature is their solvatochromic MLCT whereby, by changing the nature of the solvent, the energy of the MLCT transition can be tuned to a point lower than the corresponding ligand field excited state.

The electrochemical behavior and Mossbauer, resonance Raman and nuclear magnetic resonance spectral studies on the various such fragments have supplied valuable information in designing polymetallic complexes capable of driving useful photochemical reactions with visible light. Table I.1 summarizes such systems, their bridging ligand L and the important properties studied for these systems.

Table I.1. Bi/polymetallic Systems, Bridging ligands and their important properties studied

Sl. No.	Bi/Polymetallic System	Bridging ligand, L	Important features studied	Reference
1	2	3	4	5
1.	$[(CO)_4Cr]_2-\mu-L$	2,2'-bipyrimidine	Electronic spectra, ^{13}C NMR, photochemistry	96
2.	$[(CO)_4Mo]_2-\mu-L$	-do-	Electronic spectra, ^{13}C NMR, Redox chemistry	97
3.	$[(CO)_4W]_2-\mu-L$	-do-	-do-	96
4.	$(CO)_4Cr-L-Mo(CO)_4$	-do-	-do-	97
5.	$(CO)_4Mo-L-W(CO)_4$	-do-	-do-	97
6.	$K_4[Fe(CN)_4]_2-\mu-L$	-do-	Electronic spectra, Electrochemistry	98
7.	$[Fe(bipy)_2]_2-\mu-L^{4+}$	-do-	-do-	
8.	$[Ru(NH_3)_4]_2-\mu-L^{4+}$	-do-	-do-	99
9.	$[Ru(bipy)_2]_2-\mu-L^{4+}$	-do-	Electronic absorption and emission studies, Electrochemistry	100,101
10.	$[Ru(bipy)Cl_2]_2-\mu-L$	-do-	-do-	86
11.	$[Ru(tpy)Cl]_2-\mu-L$	-do-	-do-	86

..contd.

1	2	3	4	5
12.	$Fe^{II}-L-Cu^{II}$	-do-	Model for Fe/Cu Binuclear active site of cyctochrome c oxidase	83
13.	$[Mo(CO)_4]_2-\mu-L$	Azo-2,2'-bipyridine	Solvatochromism of MLCT	102,103
14.	$[Ru(bipy)_2]_2-\mu-L^{4+}$	4,4'-dimethyl-2,2'-bipyrimidine	Electronic absorption and emission spectra	100
15.	$[Ru(bipy)_2]_2-\mu-L^{4+}$	Biimidazole	Electronic spectra and Electrochemistry	104
16.	$[Ru(NH_3)_4]_2-\mu-L^{4+}$	Bibenzimidazole	-do-	105
17.	$[Ru(bipy)_2]_2-\mu-L^{4+}$	-do-	-do-	106
18.	$[Mo(CO)_4]_2-\mu-L$	2-Pyridine aldazine	Electronic spectra , Electrochemistry, reduction of ligand	107
19.	-do-	p-Phenylene bis(pico-linaldimine)	-do-	107
20.	-do-	p-biphenylene bis(pico-linaldimine)	-do-	107
21.	-do-	p-Xylene bis(pico-linaldimine)	-do-	107

...contd.

Table 1.1(contd.)

1	2	3	4	5
22.	$[Cr(CO)_4]_2-\mu-L$	2,3-bis(2-pyridyl)pyrazine	Electronic spectral, Electrochemical and ^{13}C NMR studies. Plot of ν_{MLCT} vs E MLCT	108
23.	$[Mo(CO)_4]_2-\mu-L$	-do-	-do-	109
24.	$[W(CO)_4]_2-\mu-L$	-do-	-do-	108
25.	$(CO)_4Mo-L-W(CO)_4$	-do-	-do-	108
26.	$(CO)_4Mo-L-Cr(CO)_4$	-do-	-do-	108
27.	$(CO)_4W-L-Cr(CO)_4$	-do-	-do-	108
28.	$K_4[Fe(CN)_5]-\mu-L$	-do-	-do-	98
29.	$[(bipy)_2Ru]_2-\mu-L^{4+}$	-do-	Electrochemistry, photochemistry	110
30.	$[Mo(CO)_4]_2-\mu-L$	2,5-bis(2-pyridyl)pyrazine	Synthesis, solvatochromism of MLCT transition	1C3
31.	$[Mo(CO)_4]_2-\mu-L$	3,6-bis(2-pyridyl)-1,2,4,5-tetrazine	Synthesis, solvatochromism of MLCT transition	102
32.	$[Ru(bipy)]_2-\mu-L^{4+}$	2,2',3,3'-tetra 2-pyridyl 6,6'-biqinoxaline	Synthesis, conductivity, redox property	104

....contd.

Table I.1 (contd.)

1	2	3	4	5
33.	$[Ru(bipy)]_2-\mu-L^{4+}$	2,3-di-2-pyridylquinoxaline	Synthesis Electrochemistry and correlation of ν_{MLCT} vs polarographic half wave potential of 1st reduction	111
34.	$[Ru(bipy)]_2-\mu-L^{4+}$	2,3,7,8-Tetra 2-pyridyl pyrazino [2,3-g]quinoxaline	Electrochemistry, correlation between the energy of MLCT transition and polarographic $\frac{1}{2}$ wave potential of 1st reduction	111
35.	$Ir(CO)(PPh_3)_2{}_2-\mu-L]-[PF_6]_2$	2-Pyridine carbaldehyde azine	Synthesis, NMR	112
36.	$Ir(CO)(PPh_3)_2-\mu-L]-[PF_6]_2$	6-Methyl 2-pyridine carbaldehyde azine	Synthesis, NMR	112
37.	$[IrCl(PPh_3)_2(\mu-L)-(\mu-NO)CuCl][PF_6]_2$	3,6 bis(2'-pyridyl)pyrazine	Synthesis and crystal structure	113

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Chapter - II

Synthesis, characterization and solvatochromic
properties of Group 6 metal carbonyls having
Schiff base of pyridine carbaldehyde as
bridging ligand

Recognition of electronic interactions between the metal
centers through a common binucleating ligand has spurred numerous
studies of bi- and multinuclear transition metal complexes. A
number of ligand bridged metal complexes have been synthesized
and studied in context of intramolecular redox processes and the
cooperative interactions between the metal centers.[1-6] Such
complexes are catalytically active in several multielectron
processes like 'water oxidation' and serve either as highly
communicative electron transfer molecular framework or directly
absorb or transfer energy.[7-14] Several complexes with σ/π donor/
acceptor ligands have been synthesized in this context.[15-24] We
therefore suppose that a study of the complexes of Group 6 (Cr,
Mo, W) metal carbonyls $[M(CO)_3L']_2L$ with binucleating Schiff base

ligands, p-phenylene bis(picolinaldimine) (hereafter referred as PBP) and p-biphenylene bis(picolinaldimine) (hereafter referred as BBP) as L and with various σ/π donor/acceptor ligands as L' will be most interesting. They can be expected to possess a large delocalized π-unsaturated ring system similar to 2,2'-bipyridine or 1,10-phenanthroline. This should exhibit a visible absorbing solvatochromic MLCT band whose positions will be susceptible to the electronic and steric properties of the ligand L' (L'=PPh_3, $AsPh_3$, $SbPh_3$, Py, Diphos).

Additionally the current involvement of the seven coordinated complexes $[MX_2(CO)_3L_2]$ [M = Mo, W; X = Cl, Br; L = PPh_3, $AsPh_3$] in catalytically ring opening polymerization of norbornene and norbornadiene[25] prompted us to examine the oxidative elimination reactions of $[M(CO)_4]_2-\mu-L$ (M = Mo, W; L = PBP, BBP). This chapter reports the syntheses, electronic (absorption, emission) and infrared spectra and their solvent depandance, electrochemistry, ^{1}H NMR and oxidative-reductive behavior of $[Mo(CO)_4]_2-$(PBP/BBP) and $[Mo(CO)_3L']_2$(PBP/BBP) complexes.

II.1 Experimental Section

(i) Materials

Metal carbonyls were purchased from Fluka Chemical Co. The ligands, p-phenylene bis(picolinaldimine)(PBP) and p-biphenylene bis(picolinaldimine)(BBP) and their complexes $[Mo(CO)_4]_2$PBP/BBP

were prepared by the literature method.[24] Pyridine 2-carbaldehyde,
p-phenylene diamine and benzidine were purchased from E. Merck,
Germany. Solvents were purified and dried before use. Elemental
analyses were performed at the Microanalytical laboratory of I.I.T.
Kanpur, India.

(ii) Instrumentation

Infra red spectra of solid samples as KBr pellets and as
solution in sodium chloride cells were taken on Perkin Elmer IR
spectrophotometer model 580.

Electronic absorption spectra were recorded on a Shimadzu
model UV-190 double beam spectrophotometer with matching quartz
cells and the emission spectra were recorded by exciting samples
using Ar^+ ion laser lines (spectraphysics 165-09) and detecting
by using a cooled PMT (C-31034) of the Spex Spectrometer. The
quantum yields of the emission could not be evaluated as the
samples underwent local burning due to high power exciting laser.

Proton ^1H NMR spectra were recorded on EM-390,90 MHz NMR
using deuterated chloroform as internal standard.

Cyclic voltammograms of the samples were obtained in dichloro-
methane solution using TBAP as supporting electrolyte. The CV
measurements were performed using a three electrode potentiostatic
circuit and a MPI model MP-1042 voltammetry controller and Plotama-
tic MF 715 X-Y recorder. A Beckman Pt electrode, a Pt wire counter

electrode and saturated calomel electrode constitute the three electrode assembly. All the potentials are referred to SCE. The redox potentials of the compounds were recorded at various scan rates from 50 mV/sec to 500 mV/sec.

The X-ray powder pattern of the samples were recorded with ISO-Debyeflex 2002 diffractometer.

The ESR spectra in tetrahydrofuran were recorded on Varian 109 E, X-band spectrometer at room temperature as well as liquid nitrogen temperature.

Preparation of Complexes

(A) $[M(CO)_4]_2$PBP/BBP (M = Cr or W)

Metal hexacarbonyl (1 mmol) and the ligand (.5 mmol) in the mole ratio of 2:1 were refluxed in 20 ml of toluene under nitrogen for 20 h whereby the color of the solution changed to dark green. The insoluble chromium compound (dark brown) was separated from solution which was washed with benzene and petroleum ether. In the case of tungsten complex a reddish brown compound was precipitated from the refluxed hot solution by the addition of petroleum ether. Though its solubility in CH_2Cl_2 or other organic solvents is small it was recrystallized by dissolving it in relatively larger volume of dichloromethane, precipitating it with petroleum ether and washed a number of times with petroleum ether. The complexes were dried _in vacuo_ and analysed (yield, _ca_ 60%).

(B)   Reaction of $[Mo(CO)_4]_2$PBP/BBP with Zn-Hg amalgam
_____

The suspension of $[Mo(CO)_4]_2$PBP/BBP (.25 mmol) in 20 ml of
tetrahydrofuran was stirred with excess of 2-3% Zn-Hg amalgam
under nitrogen atmosphere for 24 h whereupon the complex went in
solution and the color changed from violet to deep red. It was
filtered to remove Zn-Hg amalgam and other insoluble materials
(if any). The red filtrate was concentrated at reduced pressure
to about 5 ml and light petroleum ether was added to the concen-
trate. The red colored compound, thus obtained was separated by
centrifugation and dissolved in dichloromethane. The solution was
loaded on a silica gel column (100-140 mesh) of 25 cm x 2 cm dimens-
ion and was eluted slowly with dichloromethane. The red fraction
as the major band, was collected and concentrated to nearly 5 ml
at reduced pressure. Addition of petroleum ether to the concen-
trate, separated the red compound, which was filtered, washed with
petroleum ether and dried _in vacuo_ (yield, _ca_ 80%).

(C) $[Mo(CO)_3L']_2$PBP/BBP (L' = PPh_3, $AsPh_3$, $SbPh_3$, Diphos, Py)
_____

(i) To a solution of $[Mo(CO)_4]_2$PBP/BBP (.25 mmol) in 20 ml
of tetrahydrofuran an excess of the ligand L' (1.0 mmol) was added.
The mixture was refluxed under nitrogen for 24 h. The dark green
solution, thus obtained, was filtered[*] to remove insoluble

_____

[*]When L'=$AsPh_3$, $SbPh_3$, Py; the solution was filtered and worked
  up under nitrogen atmosphere.

impurities, if any, and petroleum ether was added to the filtrate, whereupon a green compound was obtained. It was recrystallized[**] from dichloromethane/petroleum ether, washed with petroleum ether and dried in vacuo. The complex was dissolved in the minimum amount of dichloromethane. The solution was loaded on a 25 cm x 2 cm diameter silica gel column (100-140 mesh) and was eluted slowly by dichloromethane. The eluate was concentrated at reduced pressure. Addition of the petroleum ether to the concentrate precipitated a green compound, which was separated by filtration, washed a number of times with petroleum ether and dried in vacuo (yield~40%).

(ii) To the tetrahydrofuran solution obtained after the Zn-Hg amalgam reaction (cf. Exptt. B) excess of the ligand L' was added and the solution was refluxed under nitrogen atmosphere for 4-5 h. The color of the solution changed to dark green. The compound was separated from the solution thus obtained by the procedure similar to that given above (yield, ca 80%).

(D) $[W(CO)_3L']_2$PBP/BBP (L'=PPh$_3$, AsPh$_3$, SbPh$_3$, Diphos, Py)

To a solution of $[W(CO)_4]_2$PBP/BBP (0.25 mmol) in 20 ml of toluene, an excess of the ligand L' (1.0 mmol) was added. This

---

[**] For L' = SbPh$_3$, Py, a little exposure to air during recrystallization decomposed the compounds immediately.

mixture was refluxed under nitrogen for 24 h. The dark green solution, thus obtained, was worked up by the procedure reported in $[(C)(i)]$ (yield, ca 40%).

(E) $[M(CO)_3I_2]_2PBP/BBP$ (M = Mo, W)

To the suspension of $[M(CO)_4]_2PBP/BBP$ (.25 mmol) in 25 ml of tetrahydrofuran, iodine (.3 mmol) was added and the solution was stirred for 4-5 h, whereby the color of the solution changed to orange brown. The resulting solution was filtered and the filtrate was concentrated to 5 ml under reduced pressure. Excess of petroleum ether was added to the concentrate whereupon orange brown microcrystalline complex was obtained. It was separated by centrifugation and recrystallized from tetrahydrofuran/petroleum ether, washed with petroleum ether and dried in vacuo (yield, ca 40%).

(F) $[M(CO)_3(HgCl)(Cl)]_2PBP/BBP$ (M = Mo, W)

To the suspension of $[M(CO)_4]_2PBP/BBP$ in 20 ml of tetra-hydrofuran, stoichiometric amount of mercuric chloride was added and the solution was stirred for 4-5 h whereby the color of the solution changed to bright orange red. The solution was filtered and the filtrate was concentrated to about 5 ml at reduced pressure Petroleum ether was added to the concentrate, whereby an orange compound separated out. It was filtered, recrystallized from

tetrahydrofuran/petroleum ether, washed with petroleum ether and dried in vacuo (yield, ca 50).

II.2   Results and Discussion

II.2a Synthesis of Complexes and their Reactivity

The synthesis of new complexes given in Table II.1 proceeds in good yield using well known literature method.[24]   The binuclear complexes of molybdenum $[Mo(CO)_4]_2$BBP/PBP have already been reported, those of tungsten and chromium $[M(CO)_4]_2$PBP/BBP which were not synthesized prior to this work, were obtained in good yield by refluxing the respective metal hexacarbonyls with PBP/BBP in toluene Attempts to prepare the complexes in benzene yielded the original reactants and the higher boiling point solvents like xylene, resulted in decomposition products.   The solubility of these complexes varies as Cr $\ll$ Mo $<$ W.   Thus chromium complexes were practically insoluble in nearly all the organic solvents, those of molybdenum, soluble in DMF and practically insoluble in CH_3OH, CH_2Cl_2 and benzene while those of tungsten, partially soluble in the same solvents.

The complexes of $[M(CO)_4]_2$PBP/BBP (M = Mo, W) reacted with four and two equivalents of iodine and mercuric chloride with the release of two molecules of CO to give Mo/W, I_2 and $HgCl_2$ derivatives, $[M(CO)_3I_2]_2$PBP/BBP and $[M(CO)_3(HgCl)Cl]_2$PBP/BBP respectively. They were found to be diamagnetic, non electrolyte, relatively

stable in air. The chemical behavior of these complexes which was similar to $[M(CO)_3(bipy)I_2]$ or $[M(CO)_3(bipy)(HgCl)Cl]$[26-28] suggested their structure as seven coordinated species. The oxidation of tetracarbonyl complexes by Br_2 resulted in the formation of possibly the complexes $[MBr_4]_2PBP/BBP$ in which metal is present in the +4 oxidation state. These compounds were highly unstable and within a couple of hours after isolation, they started becoming oil. Only analytical data, which could be obtained, were the analyses of bromide. Its IR spectra didnot exhibit any band due to carbonyl groups. We have therefore tentatively assigned its structural formula as $[MBr_4]_2PBP/BBP$.

All attempts to oxidize analogous chromium complexes using I_2, $HgCl_2$ and Br_2 as oxidants by refluxing $[Cr(CO)_4]_2PBP/BBP$ in various low and high boiling point solvents were unsuccessful. In every case the original compound was separated after the reaction was over. It is presumed that their complete insolubility in the reaction medium explains their reluctance to undergo oxidation reactions. The lack of any chemical reactivity was also observed in other reactions too as described further in this chapter.

The compounds $[M(CO)_3L']_2PBP/BBP$, where L' = PPh_3, $AsPh_3$, $SbPh_3$, Diphos, Py, were highly soluble in most of the common organic solvents except those of hydrocarbon types. They were highly air sensitive and got oxidized to an insoluble product which was analyzed as $[MO_3]_2PBP/BBP$. Their sensitivity varies as $PPh_3 \langle AsPh_3 \langle SbPh_3 \langle Py$. We were, therefore, able to isolate and store triphenylphosphine complex for a day or so. Arsine one for a couple of

hours, stibine and pyridine ones, for several minutes only. It
was therefore possible to complete our studies only on phosphine
and arsine derivatives while stibine and pyridine complexes were
partially studied. It appears that the stability of $[M(CO)_3L']_2^-$
PBP/BBP is controlled by the net charge accumulation on the metal
center by the ligand L'. The higher the negative charge developed
on the metal center, the larger it will be pulled back by the CO
through back bonding. It will result (the difference in the σ donor
and π acceptor capabilities of L') in the accumulation of negative
charge on CO which determines the instability of the M-C bond. It
is well known that the ligands PPh_3, $AsPh_3$, $SbPh_3$, Diphos and Py
are mainly σ-donor and poor π acceptor with PPh_3 being a better
donor and acceptor than $AsPh_3$ which, in turn is a better σ-donor
and π acceptor than $SbPh_3$. Py too is a very good σ-donor but poor
π acceptor. It is therefore expected that these ligands will have
a tendency to accumulate negative charge on the metal center from
where it will be transferred either to CO groups or to the PBP/BBP
through bonds. The extent of transfer of negative charge to CO
groups can be seen by lowering of the positions of ν_{CO} band in
their IR spectra. Larger lowering signifies more of electron
density at CO, consequently more instability of the complex. This
relationship in the ordering of lowering of ν_{CO} band positions with
that of the stability of the complexes is very obvious by the
comparative study of shifts of ν_{CO} band positions in their IR and
MLCT band positions in the electronic spectra of the complexes
(vide supra).

Another point of interest in these reactions is the slowness
of the thermal substitution of one of the CO groups (24 h).
Considering the partial solubility of the parent complexes (Mo in
THF) the low concentration of the complex in the reaction medium
at a time presumably explains the slowness of the reaction. Since
evidence were obtained in the literature for rapid substitution
of Lewis bases after labilizing one of the CO groups (CO cis to
PBP/BBP) by the electrochemical reduction of the analogous comple-
xes[29] attempts were made to repeat the substitution reactions by
chemically reducing the complexes using Zn-Hg amalgam. Fortunately
all the complexes dissolved in THF to give deep red colored solut-
ion after stirring the partially soluble complexes, only in the
presence of Zn-Hg analgam. From the solution after filtration of
Zn-Hg amalgam and other insoluble material, (if any), ESR inactive
(both at room temperature and liquid N_2 temperature) red complexes,
different from the original ones and highly soluble in all organic
solvents except hydrocarbon type ones were precipitated by the
dried petroleum ether. Their empirical formulae were found to be
$[M(CO)_4]_2 PBP/BBP(THF)H^+]$. In an attempt to gain further under-
standing of the reactions, the X-ray powder pattern of the red comp-
lex which gave a typical pattern of amorphous material was compared
with that of the original one (crystalline structure). The amorph-
ous compound changed to the original if kept in THF & Pet. ether
solution for a few days at low temperature (Fig. II.1). The IR
spectra exhibited bands due to ν_{NH} and THF besides the bands

originating from the original complex. In addition, the MLCT and Metal to CO charge transfer bands were shifted towards higher energy region (cf. Table II.3). Similar behavior has been observed in the literature complexes where ligand underwent reduction by the addition of electron in the π^* orbital of the ligand.[30] The MLCT band shifted from 18622 cm^{-1} in the original PBP complex to 18975 cm^{-1} in the red compound. The Metal to CO charge transfer position was also shifted from 30,000 cm^{-1} to 32,300 cm^{-1} in the red compound. Similar results were obtained in the corresponding BBP complex. Though the identity of the red compound is still not certain, the electronic spectral shift towards the higher energy region may be taken as the evidence in support of the reduction of ligand by Zn-Hg amalgam. The reason for such a blue shift has been given earlier[30] to be the localized charge of the electron on the ligand π^* LUMO, which is then transmitted via metal ion to carbonyl groups.

Accordingly, the presence of the ν_{NH} and THF bands in IR spectra, tentatively suggest that the effect of the Zn-Hg amalgam on the original complex is to produce an amorphous soluble material, possibly a reduced product, whose charge is counter balanced by H^+. The presence of NH was further confirmed by carrying out the same reactions in the presence of D_2O yielding products whose ν_{NH} band in the IR spectra was shifted to 2400 cm^{-1}. The presence of NH was also confirmed by ^1H NMR. We presume that the reasons for the enhanced activity of the red compound towards substitution

are: (1) its amorphous nature, thus reducing the lattice energy
needed for the dissolution of the complex, (2) possibly the reduced
state of ligand and thus labilizing the CO groups and (3) the
remarkably enhanced solubility of the red compound, thereby
increasing the concentration of the active species in solution
resulting in the enhanced substitution rates. We further assume
that the H^+ ions might have come from the atmospheric or absorbed
moisture on Zn-Hg amalgam or the H^+ ions from dil.sulphuric acid,
used for storage of Zn-Hg amalgam which might have adhered to the
surface of the amalgam and thus reached the reaction medium.
Unfortunately, we cannot conclusively decide the role of Zn-Hg
amalgam but it is definite that the Zn-Hg amalgam is playing some
part in labilizing the CO groups and thereby enhancing the substi-
tution rate. These assumptions, however are purely tentative.

II.2b I.R. Spectra

The infra red spectra of the tetracarbonyl complexes of
chromium and tungsten which were similar to their molybdenum analo-
gues exhibited characteristic pattern of the tetracarbonyl $[M(CO)_4]$
group in the region 2100-1800 cm^{-1} (Fig. II.2). Although the
spectral pattern of the compounds obtained after Zn-Hg amalgam
treatment didnot practically change in the carbonyl region (Table
II.1) but a new broad band assigned to ν_{NH} appeared around 3400 cm^{-1}
which was shifted to 2400 cm^{-1} on treatment with D_2O. In addition,
the spectra also exhibited five strong bands in the region of

$1350-1000$ cm^{-1} which were also mixed with those of the ligands, and a band around 2900 cm^{-1} due to ν_{CH} (Fig. II.3). These were assigned to the characteristic bands of tetrahydrofuran.[31]

Substitution of CO by a π acceptor ligand takes place at a cis position with respect to PBP/BBP[32] causing lowering of the position of ν_{CO} (Fig. II.4). The extent and the order of lowering which depend upon the nature of the incoming ligands (PPh$_3$ ≈ Diphos< AsPh$_3$ ≲ SbPh$_3$ < Py) is in concordance with the basicity (vide infra) and the stability of the complexes. The assignments of bands in $[M(CO)_4]_2$PBP/BBP and $[M(CO)_3L']_2$PBP/BBP complexes were made using the Cotton Kraihanzel method[33,34] for C_{2v} and C_s symmetry respectively (cf. Table II.1 and Appendix A.I). The spectra of all the complexes of the type $[M(CO)_3L']_2$PBP/BBP are analogous to that of $[Mo(CO)_3$bipy PPh$_3]$ in the ν_{CO} region, having the infra red active modes A and E where E mode, in general, is split into A and B.[35] This suggested that the substitution of CO by L' takes place at a cis position with respect to PBP/BBP.

The larger value of k_i in the tricarbonyl complexes compared to those of the tetracarbonyl complexes confirmed the increase in the interaction of CO groups by substituting one CO by a bulky ligand.

In general, the coordination of diimine ligand is shown by lowering of the ν_{CN} in the complexes compared to that in the free ligand.[36] In tetracarbonyl compounds the lowering in the position

of $\nu_{C=N}$ is smaller relative to that in tricarbonyl complexes. The influence of substitution of CO by L' on the π back bonding between the metal and the ligand L' is nicely manifested by further lowering of $\nu_{C=N}$ indicating a strengthening of M to L back bonding.

The study of the solvent effect on the ν_{CO} band positions indicated that the carbonyl groups trans to the ligand PBP/BBP were more influenced than the others, suggesting solvent dependent polarization in the ground state in $\pm Z$ direction[37] (Fig. II.5). As expected, the shifts in the MLCT and ν_{CO} band positions ought to be linearly dependent quantities. The MLCT band positions shifted to higher energy with the increasing polarity of the solvent (vide supra), thus enhancing the metal to carbon back bonding interaction and thereby lowering the ν_{CO} bond order.

Two major types of mechanisms are generally considered to treat the effect of the solvent upon the internal vibrations of the solute, (i) Solute molecules are assumed to be in the solvent cavities, the solvent medium being considered as a continuous continuum and (ii) Specific interactions between the solute and the solvent molecule.[38] A plot of the relative shift $\Delta\nu/\nu$ vs $(\varepsilon-1)/(2\varepsilon+1)$ where ε = static dielectric constant, exhibited reasonable linearity (Fig. II.6) which suggests that the main contribution is by the first mechanism. Thus the mechanism of the solvatochromic shift of ν_{CO} in these compounds is chiefly due to the bulk dielectric changes.

Further, it is observed from the emission spectral studies (vide supra) that with the increase in polarity of the solvent, the dipole moment of the complex with respect to its ground state varies linearly with the change in ν_{CO} in different solvents compared to that in benzene. Thus it can be inferred that as the polarity of the solvent increases the change in dipole moment is proportional to the change in ν_{CO}.

The infrared spectra of the Mo(II) iodo complexes were similar to that of the earlier reported Mo(II) iodo complexes having seven coordination[26,39,40] (Fig. II.5a). The positions of the ν_{CO} observed in the spectra of these complexes were around 2020-2030, 1970 and 1920 cm^{-1} which are characteristic positions for the other group 6 iodo complexes having seven coordination.

The spectra of the M(II) mercurous chloride showed bands due to ν_{CO} at around 1980, 1880 and 1820 cm^{-1} typical of the mercurous chloride M(II) carbonyl complexes[28] (Fig. II.7). In the reactions of mercuric chloride, it is assumed that mercuric chloride attacks the metal center as HgCl and Cl.

The infrared spectra of the brown insoluble compounds obtained after the decomposition of $[M(CO)_3L']_2PBP/BBP$ showed no bands arising due to carbonyl and coordinated ligands L' (AsPh$_3$, SbPh$_3$, etc). New intense bands, however, appear at 950 cm^{-1} and 890 cm^{-1} which can be assigned to $\nu_{M=O}$. On the basis of the microanalytical data and vibrational spectral features, the compounds were tentatively assigned the formulae $[MO_3]_2PBP/BBP$. Owing to their

insolubility in most of the common organic solvents further study on these complexes could not be carried out.

II.2c <u>Electronic absorption spectra</u>

The absorption and emission spectra of the complexes are illustrated in Fig. II.8-II.12 and the important features for the compounds $[M(CO)_4]_2$PBP/BBP and $[M(CO)_3L']_2$PBP/BBP are given in Table II.3 and II.4.

The bimetallic compounds $[W(CO)_4]_2$PBP/BBP were found to be similar to the corresponding molybdenum dimer. These compounds exhibited intense (ε>1000) solvent dependent MLCT bands in their electronic spectra. Due to the large molar absorptivity of the solvent dependent lowest energy transition and by analogy of the previously reported metal carbonyl α,α'-diimine complexes,[15-18,24,37,41-47] the lowest energy absorption of the binuclear tetracarbonyl complexes has been assigned to transition from Mdπ $\longrightarrow$ bridging ligand pπ^* (non-bonding molecular orbital to essentially π^* orbital of the ligand). As expected, the position of this band is shifted to the lower energy in going from molybdenum to tungsten complexes because of the transition of electrons to π^* orbitals of the ligand from the 5d orbitals of the tungsten which are energetically at higher energy level compared to 4d orbitals in molybdenum. The MLCT wave lengths of $[M(CO)_4]_2$PBP and $[M(CO)_4]_2$BBP are nearly equal

within the experimental observation which indicates an approximate parity of the electron withdrawing ability of PBP and BBP ligands upon the $[M(CO)_4]$ fragment. Apart from the MLCT bands, all the complexes also exhibited solvent independent band at around 380 nm which was not present in the spectra of the ligands. It has been assigned to $^1A_1$, $^1E_1 \longleftarrow ^1A_1$ ligand transition.[17,18,42,46,48,49] Though the band is absent in the spectra of the ligands, but the possibility of this transition to be mixed with the intra ligand transitions also exists.

The red compound obtained after the reaction of Zn—Hg amalgam showed MLCT band to be blue shifted compared to that present in the parent compound as discussed earlier.

Absorption spectra of the complexes $[M(CO)_3L']_2$PBP/BBP showed interesting features. Substitution of one of the carbonyls by the ligand L' (PPh$_3$, AsPh$_3$, SbPh$_3$, Py, Diphos) exhibited large influence on the position of the MLCT band. It is well known that the introduction of such a group in the complex destabilize the metal d orbitals.[32,47] Raising the metal d orbitals shifts the band to the lower energy. Additionally, the amount of destabilization of the metal d orbitals ought to be directly related to the basicity of the ligand. Any ligand capable of introducing more negative charge in the metal d orbitals will relatively destabilize the orbitals more. The shift in the MLCT band positions to the lower energy is in the order PPh$_3 \backsimeq$ Diphos $\langle$ AsPh$_3 \langle$ SbPh$_3 \langle$ Pyridine, which

is in keeping with the order of their net σ-donar and π-acceptor tendencies (cf. discussion on IR). This result is well corroborated by that of the IR spectral data of these complexes.

The positions of the MLCT absorption is strongly sensitive to the solvent used.[14,18,24,37,41-47,50] The polarity of the solvent is directly linked with the blue shift in the band position (cf. Table II.3). This solvatochromic behavior of the charge transfer transitions of related complexes has been employed by various workers to derive the various scales of solvent polarity.[51,52,45] They have defined the parameters like Donor number (DN), Reichardt Dimroth parameter (E_T), $1/Dop - 1/Ds$, E^*_{MLCT} and etc. (Table II.5) and these parameters have then been correlated with the absorption energies of L-L or L (π^*) $\longleftarrow$ M(d) of such complexes.[45-48,50,53,54]

Fig. II.13 to II.15 display the representative plots of the MLCT band positions with E_T (correlation coefficient, $R \geqslant 0.98$), with E^*_{MLCT} ($\bar{\nu} = A + BE^*_{MLCT}$; $R > 0.90$), and with donor number of the solvents ($R \geqslant .95$). They show an excellent linear correlation between the variation of the MLCT band positions with the solvent polarity and the slopes of these plots provide a relative measure of the solvent sensitivity. The slopes of the different plots of E^*_{MLCT} vs ν_{MLCT} decrease in the order Mo W. The values of the B ($B = \nu_{max}/E^*_{MLCT}$) further infer that in general tetracarbonyl complexes ($B \approx 3000$) are more sensitive towards solvent changes than the tricarbonyl complexes ($B \approx 2000$). In addition, the donor number plots show negative slope suggesting the decrease in the energy of the transition

as the donor property of the solvent increases and the intercepts give the energy of the transition when the compound is dissolved in dichloroethane.

Further a linear relationship is expected between the MLCT band positions and χ_{outer} assuming the applicability of the Hush model[55] proposed for the intervalence transfer transition.[41,50] Accordingly, the energy of MLCT band which ought to be related to the Frank Condon term (χ_{inner}) and the solvent reorientation properties (χ_{outer}) by the equation $E_{op} = \chi_{inner} + \chi_{outer} + E'_{op}$, should show linearity with the χ_{outer}. The χ_{outer} can be effectively calculated using the relationship $\chi_{outer} = (\Delta e)^2 (1/2a_1 + 1/2a_2 - 1/r) (1/Dop - 1/Ds)$ which is derived assuming the medium to be dielectric continuum. (Δe is the charge transferred, Dop and Ds are the optic and the static dielectric constants of the medium a_1, a_2 and r, the radii of the electron-donor, acceptor and distance separating them respectively). Fig. II.16 shows the plot of E_{MLCT} vs (1/Dop - 1/Ds) for one representative compound $[Mo(CO)_3PPh_3]_2PBP$ which illustrate somewhat satisfactory relationship (R = 0.85). Similar plots were also obtained with the other compounds. Though the plots are not exactly linear because of the unknown factors involved with the linear relationship but they correspond well with the literature plots.[50]

The generally observed shift to the higher energy of the MLCT transition in solvents of higher polarity has been attributed

to the ground state stabilization or the excited state destabilization of noncentrosymmetric complexes in more polar solvents. Furthermore strong solvatochromism is expected when the dissolved complex is polar. The excitation ought to be antiparallel to the ground state dipole moment. Thus, the MLCT transition induces a dipole moment in the excited state whose direction is opposed to that in the ground state. This generates a less polar situation for the complexes in the excited state. The expected stabilization of the ground state by polar solvents appear evident from the extensive blue shift of this transition in such a media, i.e. negative solvatochromism.[32,37,46,47] The red shift of the ν_{CO} of the carbonyl groups trans to the ligand suggested solvent dependent polarization in the ground state in the ± Z direction. Electron excitation in the ± Z direction must have the ground and the excited states of the same symmetry since with the given symmetry of the Z-vector, the direct product of the two identical representations of c_{2v} (assumed point group of the molecule) gives a totally symmetric integrand of the transition moment and thereby an allowed transition.

The electronic absorption spectra of the M(II) iodo complexes exhibited no bands in the visible region. However, those of mercurous chloride M(II) compounds showed a broad envelop having maxima at around 400 nm. These can be assigned as metal to ligand charge transfer transitions. As expected, the band position is insensitive to the change in solvent. The other bands below 400 nm are

assigned to the intraligand transitions and were similar to those observed in M(O) complexes as described previously.

II.2d Emission Spectra

Emission spectra of all the compounds, exhibited the usual strokes shifts which were highly sensitive to the polarity of the solvents used. The band positions shifted toward the lower energy region with the increase in solvent polarity (Table II.4). The general solvent interaction on the fluorophore molecules affecting the energy difference between the ground and the excited states is described by the Lippert's equation.[56]

$$\bar{\nu}_a - \bar{\nu}_f = 2/hc \; (\varepsilon-1)/2\varepsilon+1 \; - \; \eta^2-1/2\eta^2 + 1).(\mu^*-\mu)^2/a^3 + \text{constant}$$

where ε is the dielectric constant, η the refractive index of the solvent and a, the radius of the cavity in which the fluorophore resides. The wavenumbers in cm^{-1} of the absorption and the emission are $\bar{\nu}_a$ and $\bar{\nu}_f$ respectively. The term $[\varepsilon-1/2\varepsilon+1-\eta^2-1/2\eta^2+1]$ is generally defined as orientation polarizability, Δf. The sensitivity of a fluorophore to solvent polarity is proportional to $(\mu^*-\mu)^2$ which has been calculated by plotting Δf against the values of $(\bar{\nu}_a-\bar{\nu}_f)$. It has been observed in emission (i) that the tungsten compounds are more sensitive towards solvent polarity than those of the molybdenum and (ii) that the complexes of BBP as diimine are more sensitive than those of PBP. These results have further

been confirmed by the Lippert's plot (cf. Fig. II.17). From the slopes of the plots the magnitude of the change in dipole moments upon excitation have been calculated (Table II.4). Thus a dipole change $(\mu^* - \mu)$ by about 12 Debye units with the direction of μ^* opposite to that of the ground state dipole corresponds to a charge separation (unit charge, 4.8×10^{-10} esu) by about 2.5 A^o which is approximately a distance comparable to the size of the fluorophore. Though it is difficult to answer using present emission data, if the positive and the negative charge of the dipole are localized or delocalized over the whole molecule but approximate calculation of the magnitude of the charge separation in fluorophore during MLCT has become possible.

Furthermore, the linearity of the lippert plots suggested the dominent importance of general solvent effects in the spectral shifts rather than the specific ones.

II.2e Electrochemistry

The redox properties of these compounds obtained by using cyclic voltammetric studies are given in Table II.6. In variation to the earlier studies,[18,24,46,47] these compounds showed both the reduction as well as the oxidation processes (Fig. II.18). However, except for the compounds, $[M(CO)_4]_2$PBP/BBP; M = Mo,W; all others exhibited irreversible oxidation waves in the anodic scan with no return cathodic waves. These may be attributed to the one electron

oxidation of the metal center[17,46,47] in which case the resulting Mo(I) complexes are unstable. This has also been observed earlier for similar systems.[17,46,47] Furthermore, in going from molybdenum to tungsten complexes, oxidation potential decreases suggesting easier oxidizability of tungsten compared to that of molybdenum. Similar conclusion was also derived by the study of the MLCT band position in the two cases. The position of MLCT band in the tungsten complexes was found to be shifted towards lower energy (easy oxidizability) compared to that of molybdenum complexes.

The effect of substitution of one CO by triphenylphosphine lowers considerably ($\sim$.1 - .2v) the oxidation potential of the metal ions. These complexes showed typical cyclic voltammograms where reversibility observed in the tetracarbonyl systems is generally lost as expected.[47]

Apart from the oxidation, these compounds also displayed reduction process at potentials ranging from -1.0 to -1.4 V. These are attributed to the reduction of the ligands. The reductions shown by $[M(CO)_4]_2$PBP/BBP are quasireversible while the corresponding phosphine substituted derivatives showed the irreversible ones with the absence of the corresponding anodic waves in the return scan.

The energy of the MLCT absorption maximum which is dependent upon the ease of oxidation of the central metal ions ought to have a direct relationship with the potentials obtained by cyclic voltammetry. It is obvious from Table II.6 that the trend is towards

an increase of oxidation potential as the energy of MLCT transition
increase implying the order of metal molecular orbital stabilizat-
ion as W < Mo. A quantitative assessment of the electrochemistry
corresponding to the compounds listed in Table II.6 agrees with
the energetic ordering. The red shift of the MLCT transition in
W-L-W compared to that in molybdenum analogue indicates that the
HOMO of the bimetallic tungsten complexes is destabilized with
respect to the analogoues molybdenum complexes (vide infra) (HOMO's
in the complexes contain a very large contribution from the metal
dπ orbitals). Cyclic voltammetric experiments indicated that the
oxidation potential of the tungsten tetracarbonyl complexes was
less than the molybdenum complexes implying destabilization of the
tungsten orbitals compared to molybdenum ones. This result is in
concordance with the observed absorption spectral pattern. Further-
more, the substitution of phosphine further lowers the oxidation
potential of the metal. Thus compared to the tetracarbonyl system,
the tricarbonyl phosphine derivatives have the oxidation potential
lower by .1 - .2v indicating that the phosphine derivatives can be
more easily oxidized compared to the tetracarbonyl compounds which
supports our earlier results (vide infra). The lowering of the
oxidation potential of the metals in $[M(CO)_3L']_2$PBP/BBP may also
explain tentatively very high susceptibility of these complexes
towards oxidation.

It is interesting to note that in going from PBP to BBP complexes, the oxidation potential increases slightly, a trend opposite to the expected one because of the larger delocalization of orbitals in BBP. This tendency towards higher oxidation potential in BBP could be due to the possible decreased conjugation in BBP assuming the non-planarity of the two phenyl rings. This is also supported by the value of the conproportionation constants for the binuclear complexes $[Mo(CO)_4]_2$PBP/BBP which decreases in the order PBP > BBP[24] indicating the decreased interaction of the two M-α,α' diimine moieties in BBP complexes compared to that in PBP ones.

II.2f ^{1}H NMR

The ^{1}H NMR spectra of the complexes and the free ligands showed coordination of the ligand (Table II.7). Owing to the insolubility or very little solubility of $[M(CO)_4]_2$PBP/BBP in common organic solvents, their spectra could not be obtained. However the NMR spectra of the red compound obtained after the reaction of Zn-Hg amalgam displayed a shift on coordination in the resonances at 8.35 and 8.7 towards higher fields (at 8.4 and 9.2 ppm respectively).[32] Besides a hump was observed around 5-6 ppm assignable to N-H which disappeared on deuteration. Two peaks at around 1.8 and 3.75 ppm are assigned to the tetrahydrofuran protons.

The NMR spectra of $[M(CO)_3PPh_3]_2PBP/BBP$ showed similar features for the ligand except that there appeared resonances due to triphenyl phosphine protons also.

Such type of compounds are also known to exhibit solvent dependent NMR[37] but due to low solubility of the compounds, no efforts have been made in this direction.

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Table II.1a Microanalytical and Infrared spectral data of the compounds [M(CO)₄]₂PBP/BBP

S.No.	Compounds	Color	C	H	N	M	νCO cm⁻¹				mdyne/A°			δ M-C-O	νC=N
							$A_1(1)$	$A_1(2)$	B_1	B_2	k_1	k_2	k_1		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1.	[Mo(CO)₄]₂PBP(R)	R	44.6 (44.5)	2.0 (2.0)	8.1 (8.0)	26.8 (27.4)	2010	1865 (1852)	1910	1820	13.7	15.4	.34	610,590, 550	1604
2.	[Mo(CO)₄]₂BBP(R)	R	49.1 (49.4)	2.4 (2.3)	7.4 (7.2)	23.7 (24.6)	2000	1870 (1870)	1900	1830	13.85	15.34	.36	610,585, 540	1604
3.	[Cr(CO)₄]₂PBP	B	50.2 (50.9)	3.1 (2.3)	8.9 (9.1)	16.5 (16.9)	2000	1870 (1879,3)	1900	1830	13.85	15.34	.36	640,550	1602
4.	[Cr(CO)₄]₂BBP	BB	55.8 (55.8)	3.2 (2.6)	7.8 (8.1)	14.7 (15.1)	2010	1860 (1848)	1910	1835	13.85	15.3	.29	640,550	1602
5.	[W(CO)₄]₂PBP	RB	35.2 (35.6)	2.5 (1.6)	6.1 (6.4)	41.2 (42.0)	2000	1860 (1862)	1900	1830	13.70	15.27	.34	635,540	1608
6.	[W(CO)₄]₂BBP	RB	39.8 (40.2)	2.5 (1.9)	5.2 (5.9)	39.1 (38.6)	2000	1860 (1860)	1900	1830	13.83	15.27	.34	640,545	1608

Table II.1b Microanalytical and Infrared spectral data of the compounds [M(CO)₃L']PBP/BBP

S.No.	Compounds	Color	C	H	N	M	νCO cm⁻¹			mdyne/A°			δ M-C-O	νC=N
							$A_1(2)$	$A_1(1)$	B	k_1	k_2	k_1		
1.	[Mo(CO)₃PPh₃]₂PBP	G	60.9 (61.6)	4.5 (3.8)	4.2 (4.8)	16.0 (16.5)	1930	1810	1840	13.66	14.10	.45	630,600, 510	1590
2.	[Mo(CO)₃PPh₃]₂BBP	G	63.2 (63.7)	4.3 (3.8)	3.9 (4.5)	15.2 (15.4)	1920	1800	1832	13.52	13.99	.445	635,595, 515	1590
3.	[W(CO)₃PPh₃]₂PBP	G	54.1 (53.5)	4.1 (3.3)	3.9 (4.2)	26.8 (27.3)	1920	1800	1830	13.53	13.97	.455	625,590, 510	1595
4.	[W(CO)₃PPh₃]₂BBP	G	55.1 (55.7)	4.2 (3.4)	3.5 (3.9)	25.1 (25.9)	1925	1800	1830	13.56	13.99	.477	625,590, 570	1595
5.	[Mo(CO)₃Diphos]₂PBP	G	62.9 (63.2)	4.5 (4.3)	3.5 (3.9)	13.1 (13.3)	1920	1800	1840	13.41	14.06	.41	630,600, 500	1590
6.	[Mo(CO)₃Diphos]₂BBP	G	64.2	4.7	3.2	12.0	1920	1810	1840	13.61	14.07	.407	630,600, 510	1590

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
7.	[W(CO)$_3$Diphos]$_2$PBP	G	55.8 (56.4)	4.2 (3.8)	3.2 (3.5)	21.9 (22.7)	1922	1802	1840	13.5	14.06	.407	620, 585, 500	1595
8.	[W(CO)$_3$Diphos]$_2$BBP	G	57.5 (58.0)	4.3 (3.9)	3.0 (3.3)	21.2 (21.7)	1920	1805	1840	13.5	14.07	.407	620, 580, 500	1595
9. *	[Mo(CO)$_3$AsPh$_3$]$_2$PBP	G					1910	1800	1835					
10. *	[Mo(CO)$_3$AsPh$_3$]$_2$BBP	G					1910	1805	1835					
11. *	[W(CO)$_3$AsPh$_3$]$_2$PBP	G					-	-	-					
12. *	[W(CO)$_3$AsPh$_3$]$_2$BBP	G					-	-	-					
13. *	[Mo(CO)$_3$SbPh$_3$]$_2$PBP	G					1900	1800	1830					
14. *	[Mo(CO)$_3$SbPh$_3$]$_2$BBP	G					1900	1800	1830					
15 *	[W(CO)$_3$SbPh$_3$]$_2$PBP	G					-	-	-					
16 *	[W(CO)$_3$SbPh$_3$]$_2$BBP	G					-	-	-					
17 *	[Mo(CO)$_3$Py]$_2$PBP	G					1890	1740(br)	-					
18 *	[Mo(CO)$_3$Py]$_2$BBP	G					1890	1740(br)	-					
19 *	[W(CO)$_3$Py]$_2$PBP	G					-	-	-					
20 *	[W(CO)$_3$Py]$_2$BBP	G					-	-	-					

* Unstable compounds

Color: R, Red; RB, Red Brown; BB, Brown Black; G, Green.

$A_1^{(1)}$, $A_1^{(2)}$, B_1, B_2 and $A_1^{(2)}$, $A_1^{(1)}$ and B are the symmetry species for the vibrational modes of CO [35,34]

k_1, k_2, k_1 are force constants.

S.No.	Compounds	Color	C	H	N	Cl	M	CO	M-C-O	C≡N
1.	[Mo(CO)$_3$I$_2$]$_2$PBP	OB	25.1 (24.9)	1.8 (1.2)	4.5 (4.9)	44.2 (44.0)	15.9 (16.6)	2010, 1970, 1915	600	1600
2.	[Mo(CO)$_3$I$_2$]$_2$BBP	OB	28.8 (29.2)	1.9 (1.5)	4.2 (4.6)	41.1 (41.3)	15.3 (15.6)	2030, 1975, 1935	595	1600
3.	[W(CO)$_3$I$_2$]$_2$PBP	OB	22.2 (21.6)	1.3 (1.0)	3.9 (4.2)	37.9 (38.2)	27.2 (27.7)	2030, 1970, 1920	595	1600
4.	[W(CO)$_3$I$_2$]$_2$BBP	OB	25.1 (25.6)	1.8 (1.3)	3.8 (4.0)	35.8 (36.1)	26.8 (26.2)	2025, 1975, 1925	590	1600
5.	[Mo(CO)$_3$(HgCl)Cl]$_2$PBP	O	23.8 (24.2)	1.6 (1.2)	4.2 (4.7)	11.8 (12.0)	15.9 (16.1)	1980, 1880(br)	590	1610
6.	[Mo(CO)$_3$(HgCl)Cl]$_2$BBP	O	28.1 (28.5)	1.7 (1.4)	4.2 (4.4)	10.8 (11.2)	15.0 (15.2)	1985, 1880(br)	585	1610
7.	[W(CO)$_3$(HgCl)Cl]$_2$PBP	O	20.9 (21.1)	1.7 (1.0)	4.1 (4.1)	10.1 (10.4)	27.1 (27.0)	1980,1875(br),1820(sh)	590	1595
8.	[W(CO)$_3$(HgCl)Cl]$_2$BBP	O	24.7 (25.0)	1.9 (1.3)	3.7 (3.9)	10.2 (9.8)	25.2 (25.5)	1980,1880(br)1820(sh)	580	1595

OB, Orange Brown; O, Orange.

Table II.2 Solvent dependance of ν_{CO}.

Solvent	$[\text{Mo(CO)}_3\text{PPh}_3]_2\text{PBP}$		$[\text{Mo(CO)}_3\text{PPh}_3]_2\text{BBP}$	
Carbon tetrachloride	1945	1850	1935	1840
Benzene	1945	1850	1935	1840
Chloroform	1936	1840	1925	1838
Tetrahydrofuran	-	-		
Dichloromethane	1936	1840	1925	1838
Acetone	1934	1835	1922	1835
Acetonitrile	1925	1835	1920	1830

Table II.3a Electronic Spectral Data of $[M(CO)_4]_2\mu$-L Compounds (M=Mo,W; L=PBP,BBP)$\lambda_{max,nm}$ (MLCT).

Solvent	$[Mo(CO)_4]_2PBP$	$[Mo(CO)_4]_2BBP$	$[Mo(CO)_4]_2PBP(R)$	$[Mo(CO)_4]_2BBP(R)$	$[W(CO)_4]_2PBP$	$[W(CO)_4]_2BBP$
Benzene	I	I	540	540	570	570
Chloroform	I	I	535	533	560	565
Tetrahydrofuran	537	537	527	525	560	560
Dichloromethane	I	I	527	525	555	550
Acetone	I	I	515	508	525	520
Benzonitrile	I	I	d	d	d	d
Acetonitrile	I	I	510	495	515	510
Dimethylformamide	507	505	d	d	d	d

I = insoluble; d = decomposed.

Table II.3b Electronic Spectral Data of $[M(CO)_3PPh_3]_2\mu-L$ Compounds $[M=Mo,W; \quad L=PBP,BBP]$ $\lambda_{max,nm}$ (MLCT)

Solvents	$[Mo(CO)_3PPh_3]_2PBP$	$[Mo(CO)_3PPh_3)_2BBP$	$[W(CO)_3PPh_3]_2PBP$	$[W(CO)_3PPh_3]_2PBF$
Benzene	640	640	650	650
Chloroform	625	625	630	630
Tetrahydrofuran	625	620	d	d
Dichloromethane	620	620	625	625
Acetone	605	605	610	610
Benzonitrile	610	610	605	605
Acetonitrile	585	580	585	590
Propylenecarbonate	580	580	580	585

d = decomposed.

Table II.3c Electronic spectra of $[M(CO)_3L']_2PBP/BBP$ (M=Mo,W; L'=AsPh$_3$, SbPh$_3$, Diphos, Py) λ_{max} (MLCT) in nm.

S.No.	Compounds	Benzene	Dichloromethane	Acetonitrile
1.	$[Mo(CO)_3AsPh_3]_2PBP$	650	635	d
2.	$[Mo(CO)_3AsPh_3]_2BBP$	650	630	d
3.	$[W(CO)_3AsPh_3]PBP$	655	640	610
4.	$[W(CO)_3AsPh_3]BBP$	655	635	d
5.	$[Mo(CO)_3SbPh_3]_2PBP$	655	d	d
6.	$[Mo(CO)_3SbPh_3]_2BBP$	655	d	d
7.	$[W(CO)_3SbPh_3]_2PBP$	660	d	d
8.	$[W(CO)_3SbPh_3]_2BBP$	660	660	585
9.	$[Mo(CO)_3Py]_2PBP$	720	665	580
10.	$[Mo(CO)_3Py]_2BBP$	720	665	d
11.	$[W(CO)_3Py]_2PBP$	725	665	d
12.	$[W(CO)_3Py]_2BBP$	725	d	d

d = decomposed.

Table II.4 Emission spectral data of few compounds: λ_{max} in cm^{-1}

Compound	Dichloromethane	Acetone	Acetonitrile	$(\dfrac{\mu^*-\mu}{a^{3/2}})$
$[Mo(CO)_3PPh_3]_2PBP$	15,400	15,302	15,095	7.46
$[Mo(CO)_3PPh_3]_2BBP$	14,200	14,200	13,800	10.56
$[W(CO)_3PPh_3]_2PBP$	14,000	13,850	13,600	10.6
$[W(CO)_3PPh_3]_2BBP$	13,935	13,800	13,500	11.1

Table II.5 Solvent Parameters

Solvent	D_s	D_{op}	$\left[\dfrac{1}{D_{op}} - \dfrac{1}{D_s}\right]$	$\dfrac{D_s - 1}{2D_s + 1}$	η_D^{20}	E_T	DN	E^*_{MLCT}
Benzene	2.27	2.24	.005	.23	1.5010	34.5	0.1	0.34
Chloroform	4.7	2.085	.267	.36	1.4460	39.1	-	0.42
Tetrahydrofuran	7.4	1.971	.37	.41	1.4070	37.4	20.0	.59
Dichloromethane	8.9	2.028	.38	.42	1.4240	41.1	-	.67
Acetone	20.7	1.84	.495	.46	1.3585	42.2	17.0	0.82
Benzonitrile	25.2	2.34	.39	.47	1.5280	42.0	11.9	
Acetonitrile	36.2	1.8	.53	.48	1.3440	46.0	14.1	0.98
Propylene Carbonate	65.1	2.01	.48	.49	1.4210	46.6	15.1	

Table II.6 Redox behavior of $[M(CO)_4]_2PBP/BBP$ and $[M(CO)_3PPh_3]_2PBP/BBP$ complexes $[M = Mo, W]$.

Compound	Oxidation	Reduction
$[Mo(CO)_4PBP$	+ 1.02 (Pt) (50) + .8 (GC) (40)	−1.34 (160) (Pt)
$[Mo(CO)_4]_2BBP$	+ 1.04 (50) (Pt) + .87 (60) (GC)	−1.4 (160) (Pt)
$[W(CO)_4]_2PBP$	.8. (70) (Pt)	−1.27 (200)(Pt) Two waves overlapping
$[W(CO)_4]_2BBP$	.8 (80) (Pt)	−1.160(120)(GC) 50 −1.165(170)(GC) 100 −1.175(190)(GC) −1.31 (150)(Pt) 200
$[Mo(CO)_3PPh_3]_2PBP$	+ .78(anodic)(Pt)	− .82 (cathodic)
$[Mo(CO)_3PPh_3]_2BBP$	+ .84(anodic)(Pt)	−1.1 (cathodic)
$[W(CO)_3PPh_3]_2PBP$	+ .72 (70) (Pt)	− .74 (cathodic) −1.28 (cathodic)
$[W(CO)_3PPh_3]_2BBP$	+ .75 (anodic)(Pt)	−1.1 (cathodic)

Table II.7 Proton N.M.R. Data (ppm) for the free ligands and the complexes.

Structure	Ligand	$[Mo(CO)_4]_2\mu L$	$[Mo(CO)_3PPh_3]_2\mu -$
	5 8.35	8.45	8.4
			8.75
	10 8.79	9.2	9.2
	5 8.3	8.49	8.42
			8.70
	10 8.78	9.22	9.20

1 [Mo(CO)₄]₂ PBP
2 [Mo(CO)₄]₂ PBP after Zn-Hg reaction
3 [Mo(CO)₄]₂ PBP obtained from the
solution of Zn-Hg amalgam reaction
after keeping it for ten days
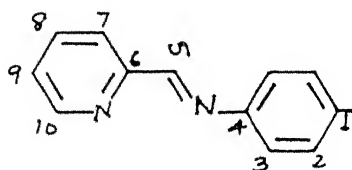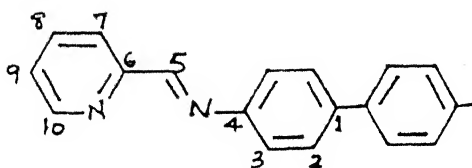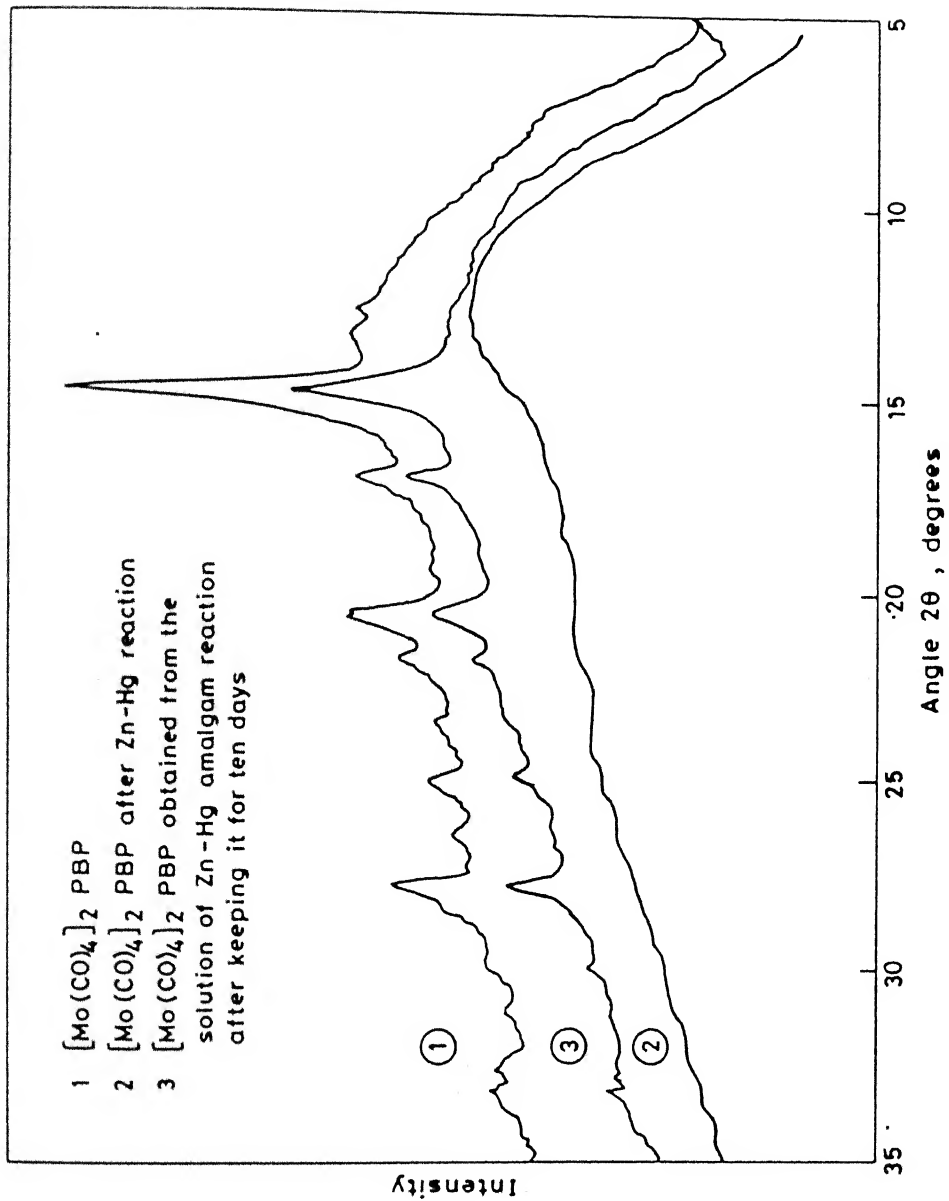
Fig.II.1 X-ray powder patterns.
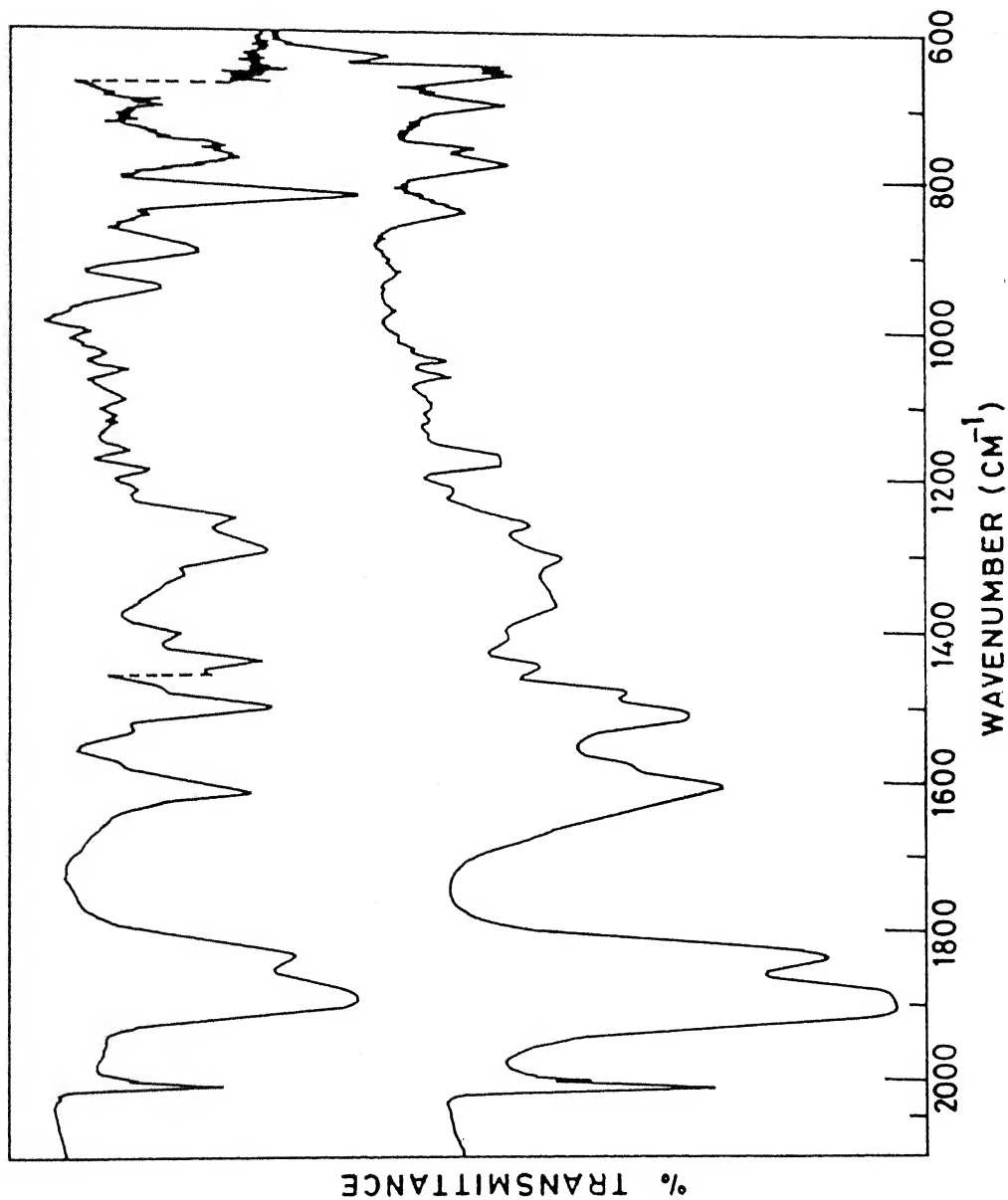
Fig.II.2 Infrared spectra of $[Cr(CO)_4]_2-\mu-PBP$ (upper) and $[W(CO)_4]_2-\mu-BBP$ (lower).
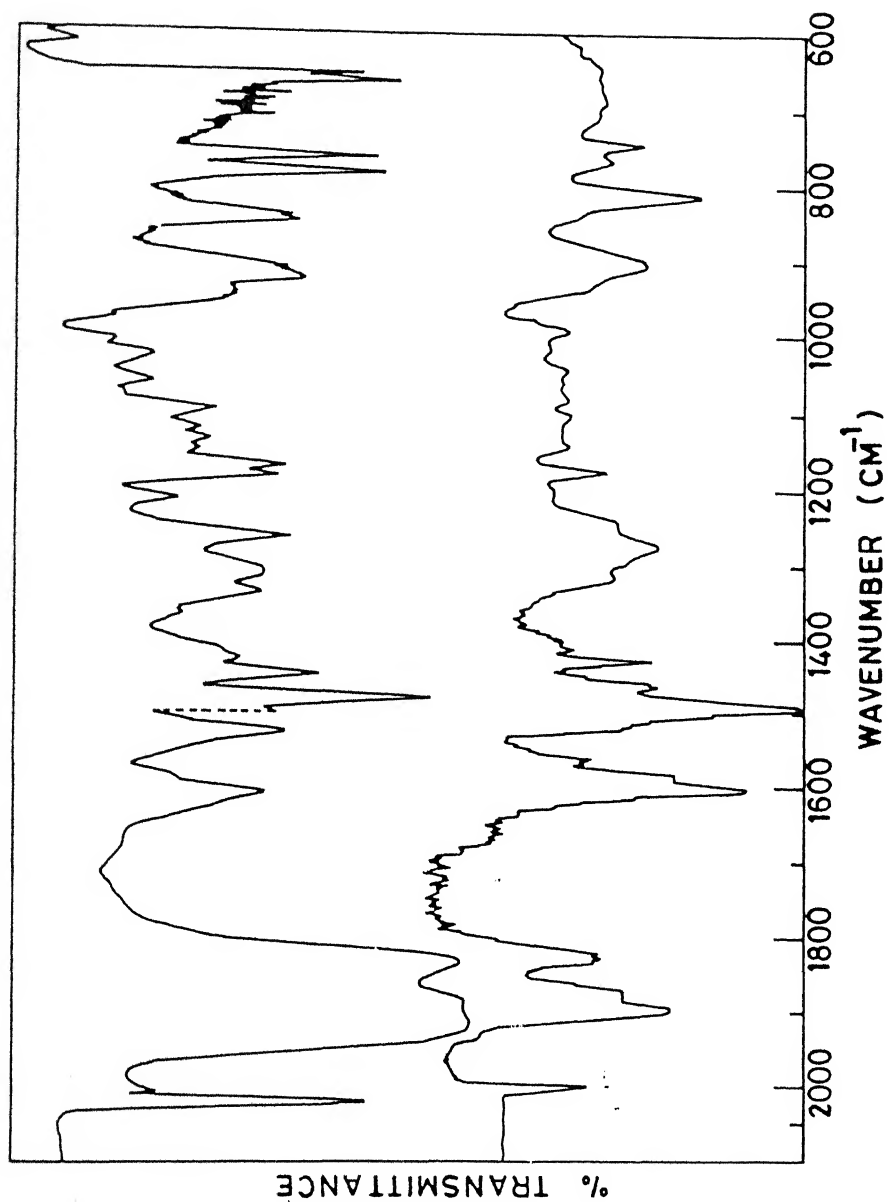
Fig.II.3 Infrared spectra of $[Mo(CO)_4]_2-\mu-PBP$ (upper) and $[Mo(CO)_4]_2-\mu-BBP$ (lower) after Zn-Hg reaction.
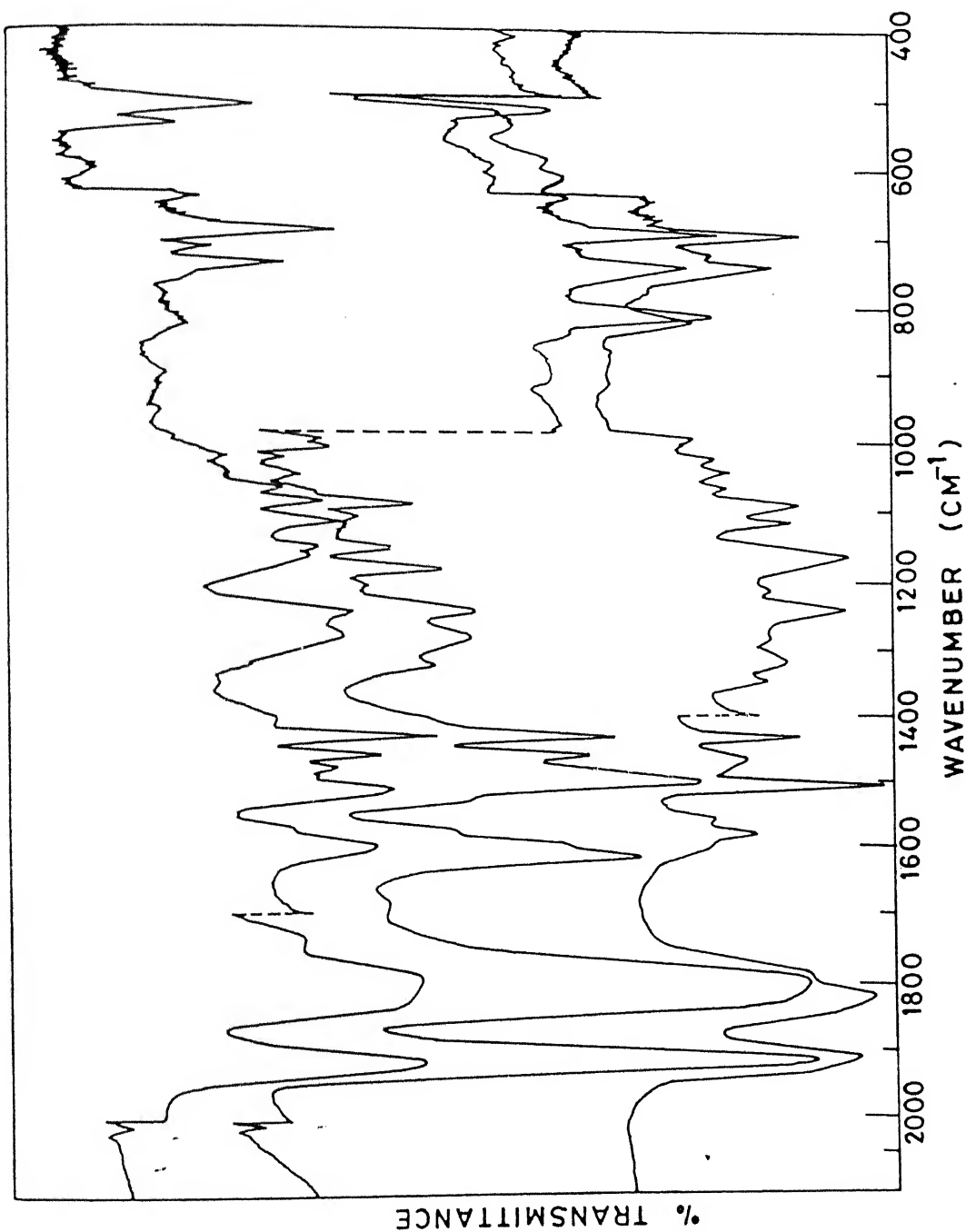
Fig.II.4 Infrared spectra of $[Mo(CO)_3PPh_3]_2-\mu-PBP$ (upper), $[W(CO)_3PPh_3]_2-\mu-PBP$ (middle) and $[Mo(CO)_3Diphos]_2-\mu-PBP$ (lower).
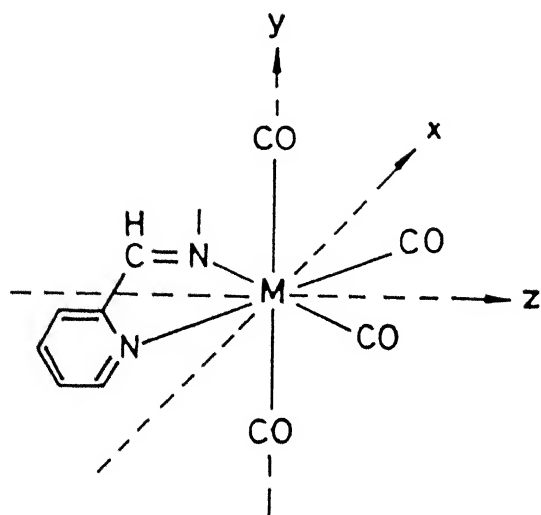
Fig.II.5 Proposed structure of $[M(CO)_4]_2-\mu-L$.
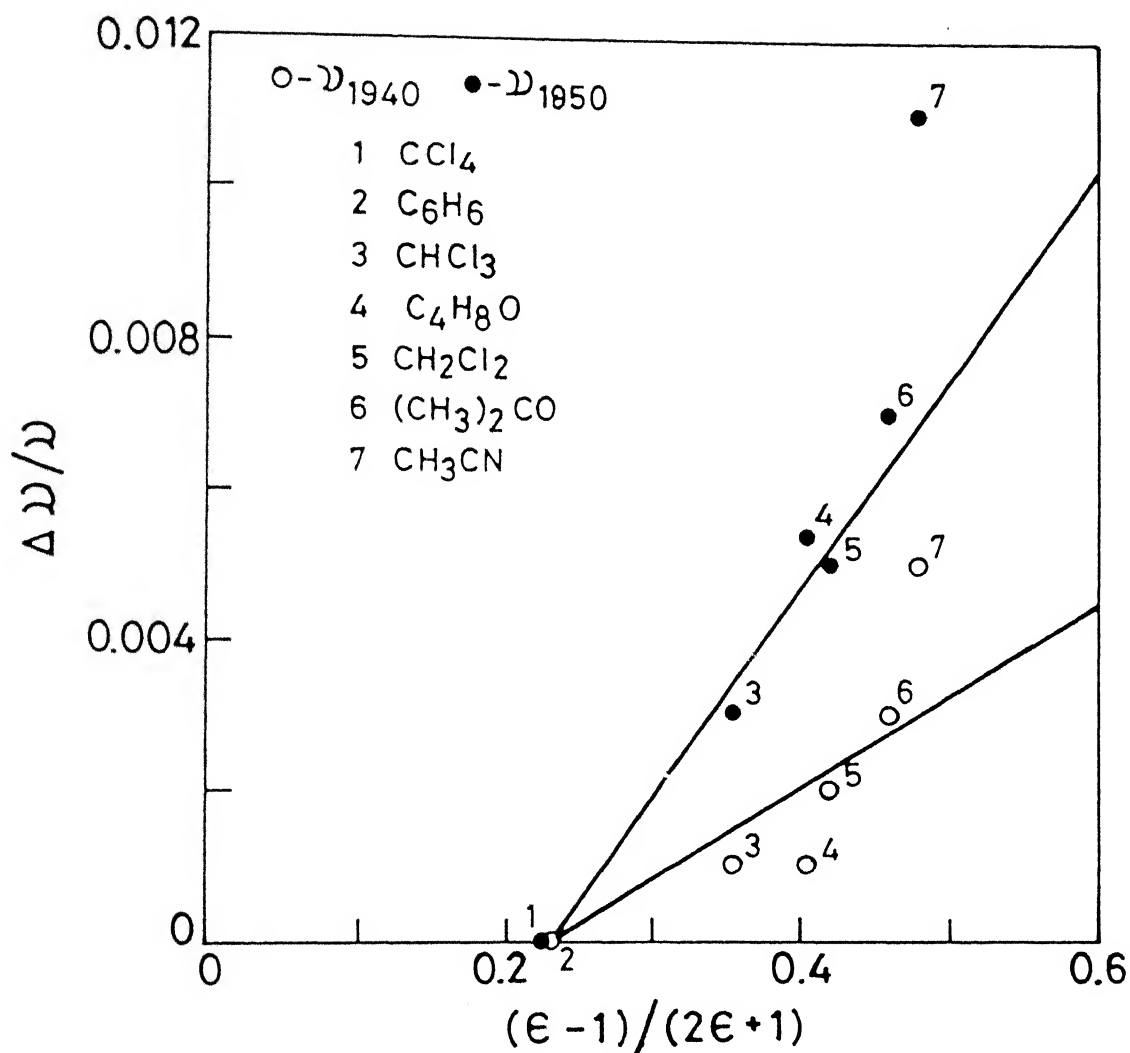
Fig.II.6 Plot of $\Delta v/v$ vs $(\varepsilon-1)/(2\varepsilon+1)$ for the ν_{CO} of $[Mo(CO)_3PPh_3]_2PBP$.
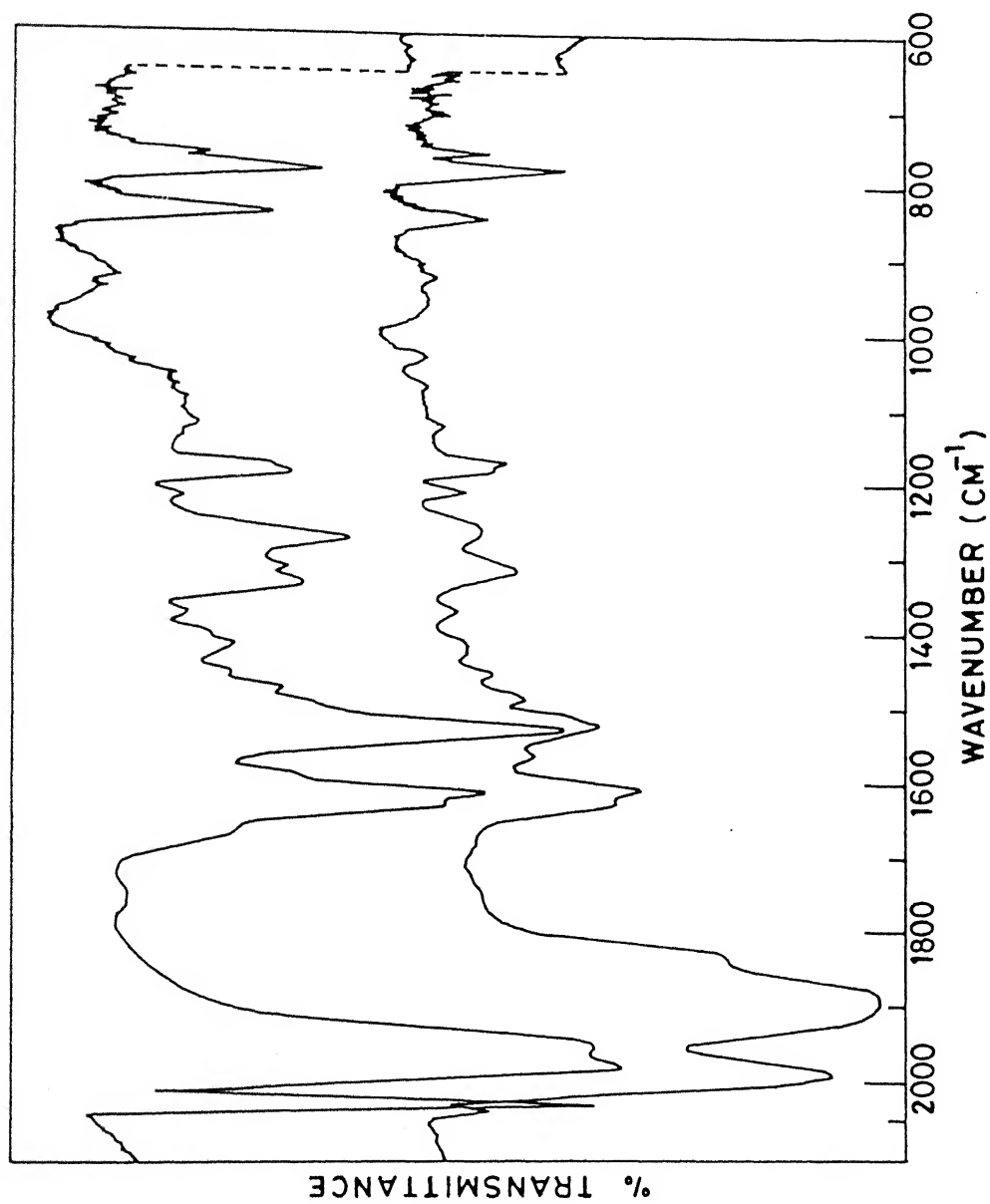
Fig.II.7 Infrared spectra of $[Mo(CO)_3I_2]_2$–μ–PBP (upper) and $[Mo(CO)_3(HgCl)Cl]_2$–μ–PBP (lower).

EMISSION

ABSORBANCE

WAVELENGTH (NM)

537.63

877.19

500   600   700   800

C_6H_6

$CHCl_3$

CH_2Cl_2

$(CH_3)_2CO$

CH_3CN

C_6H_5CN

PC

C_4H_8O
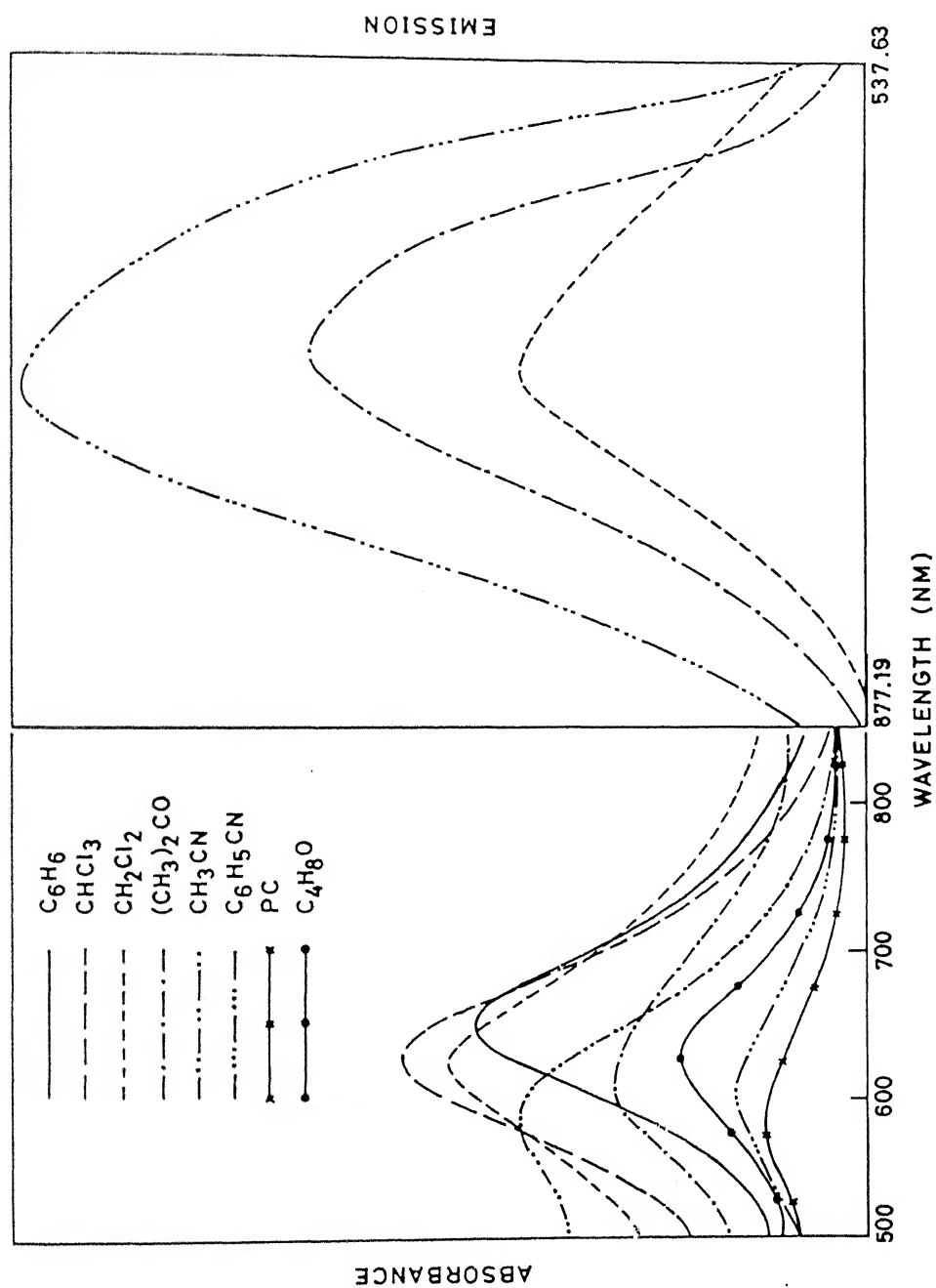
Fig.II.8 Absorption and Emission spectra of $[Mo(CO)_3 PPh_3]_2$-μ-PBP.
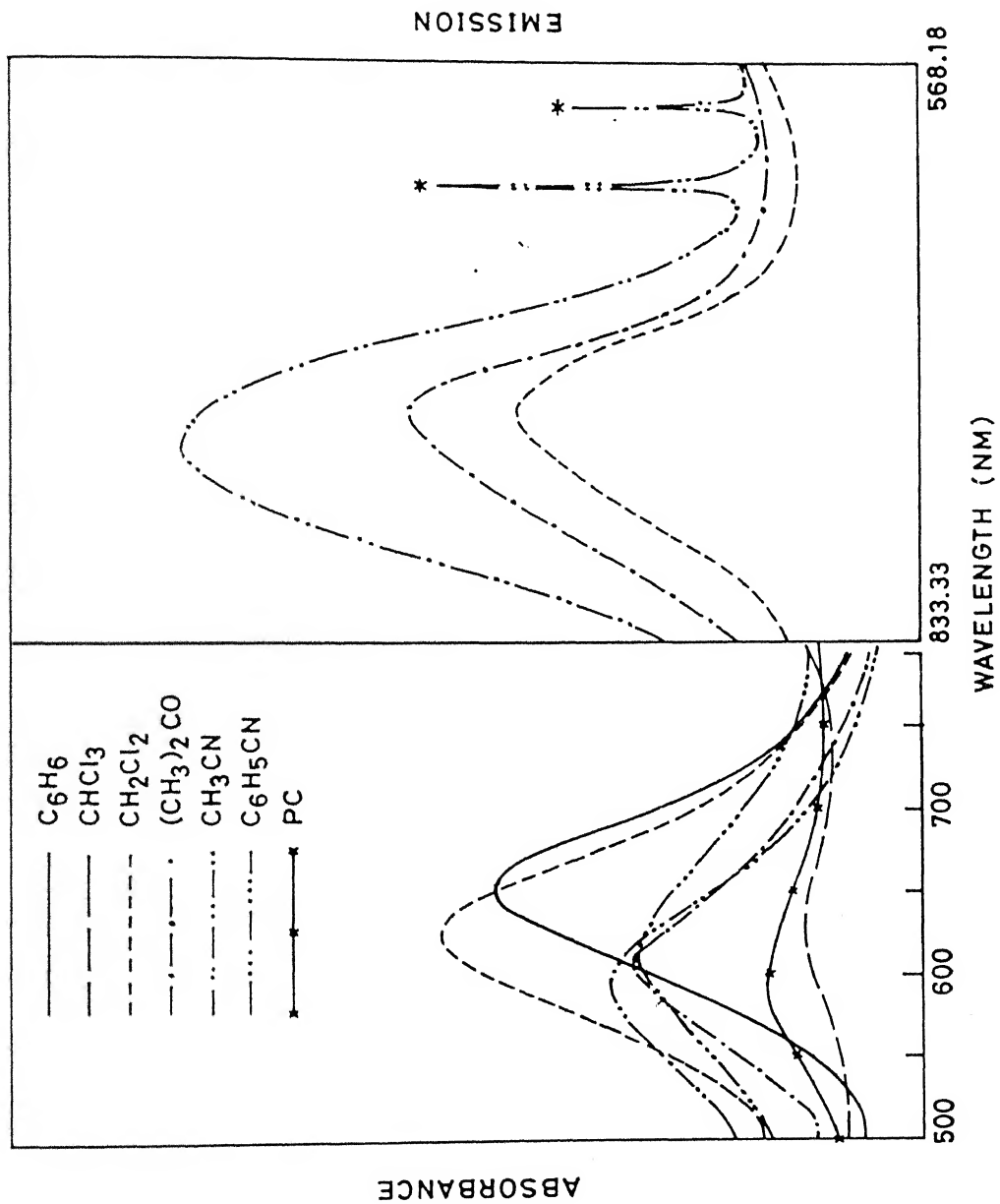
Fig. II.9 Absorption and Emission spectra of $[Mo(CO)_3 PPh_3]_2-\mu-BBP$.
*Solvent peaks.
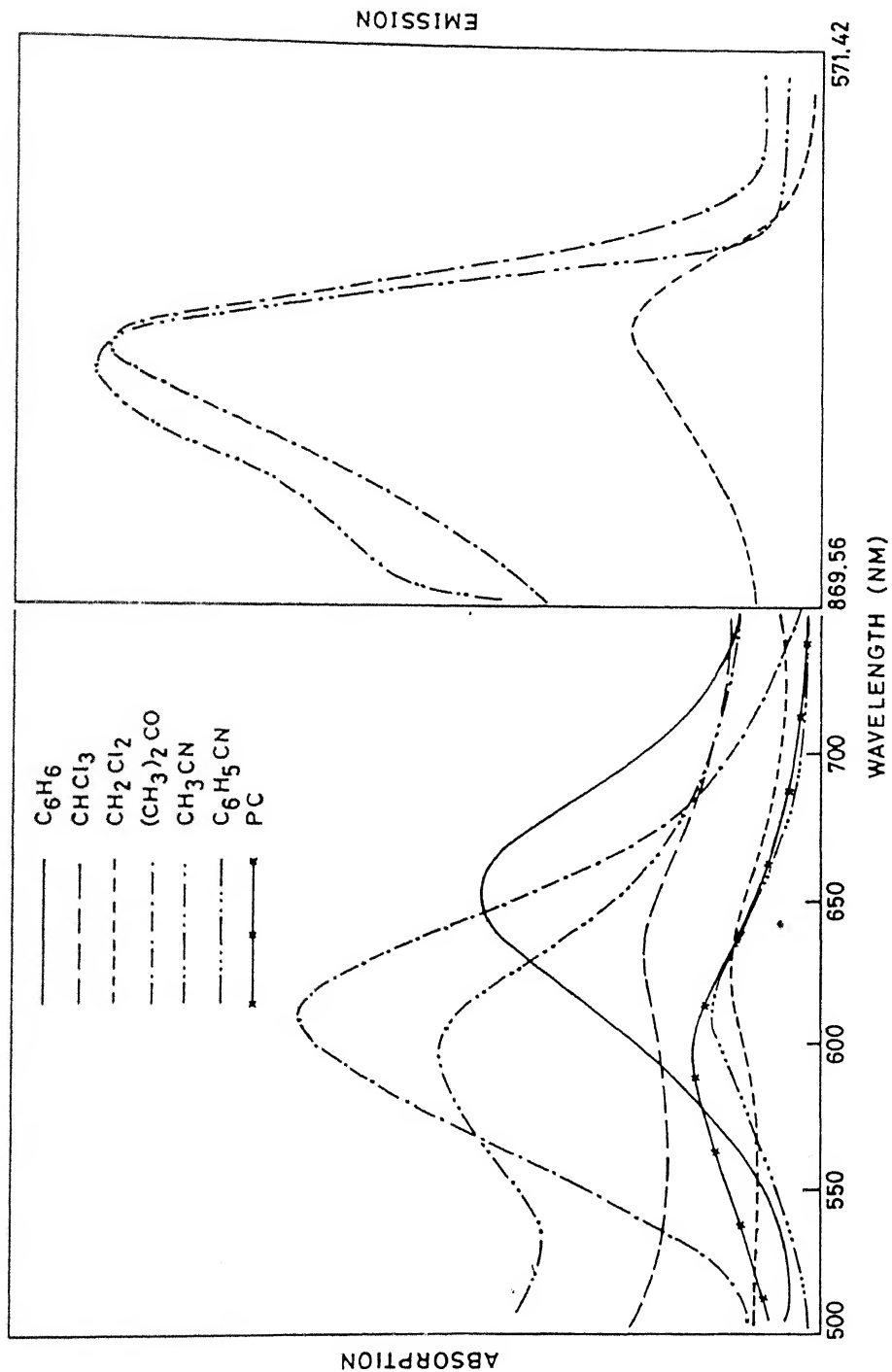
Fig.II.10 Absorption and Emission spectra of $[W(CO)_3PPh_3]_2$–μ–PBP.
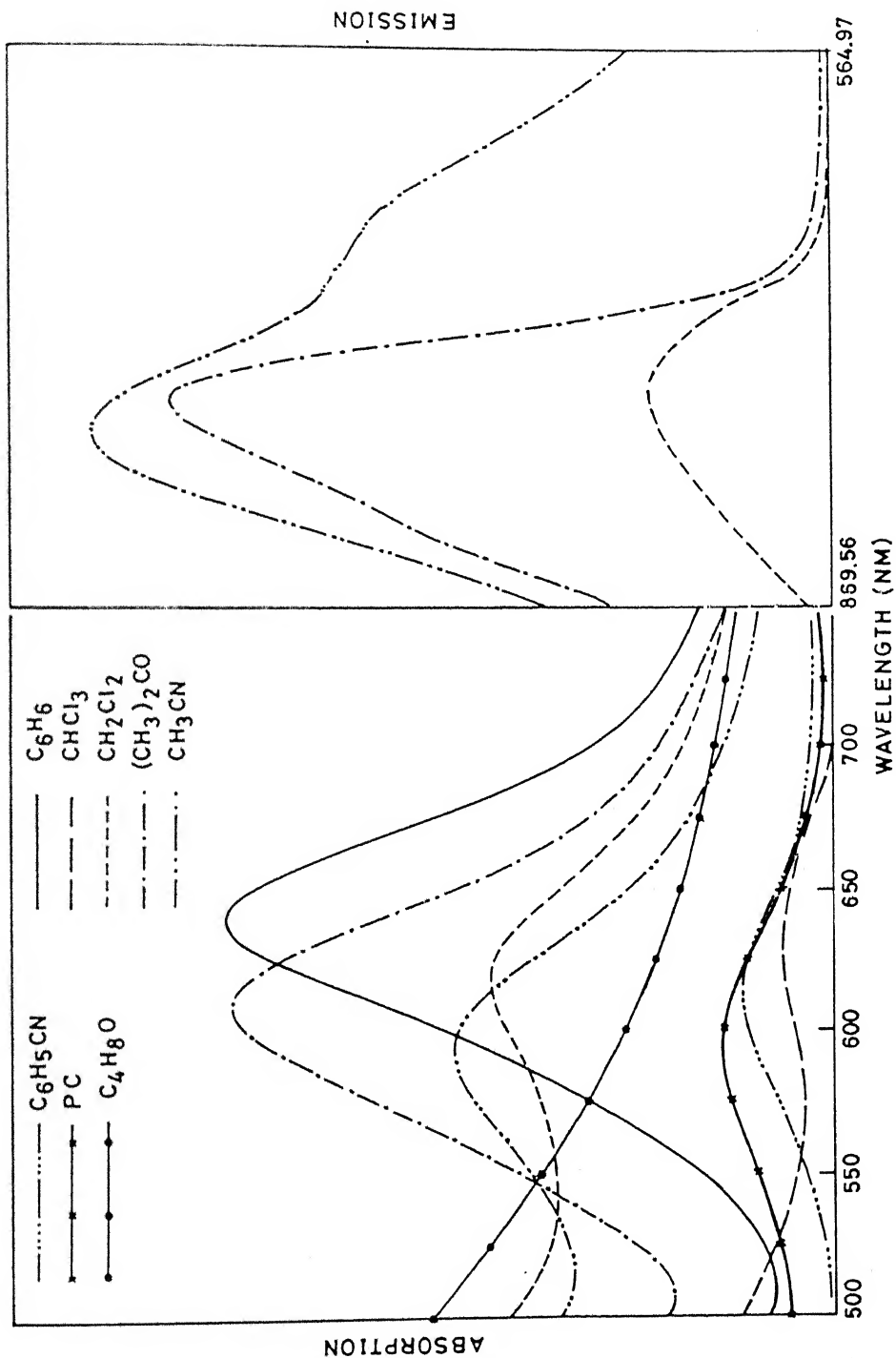
Fig.II.11 Absorption and Emission spectra of $[W(CO)_3PPh_3]_2$-μ-BBP.
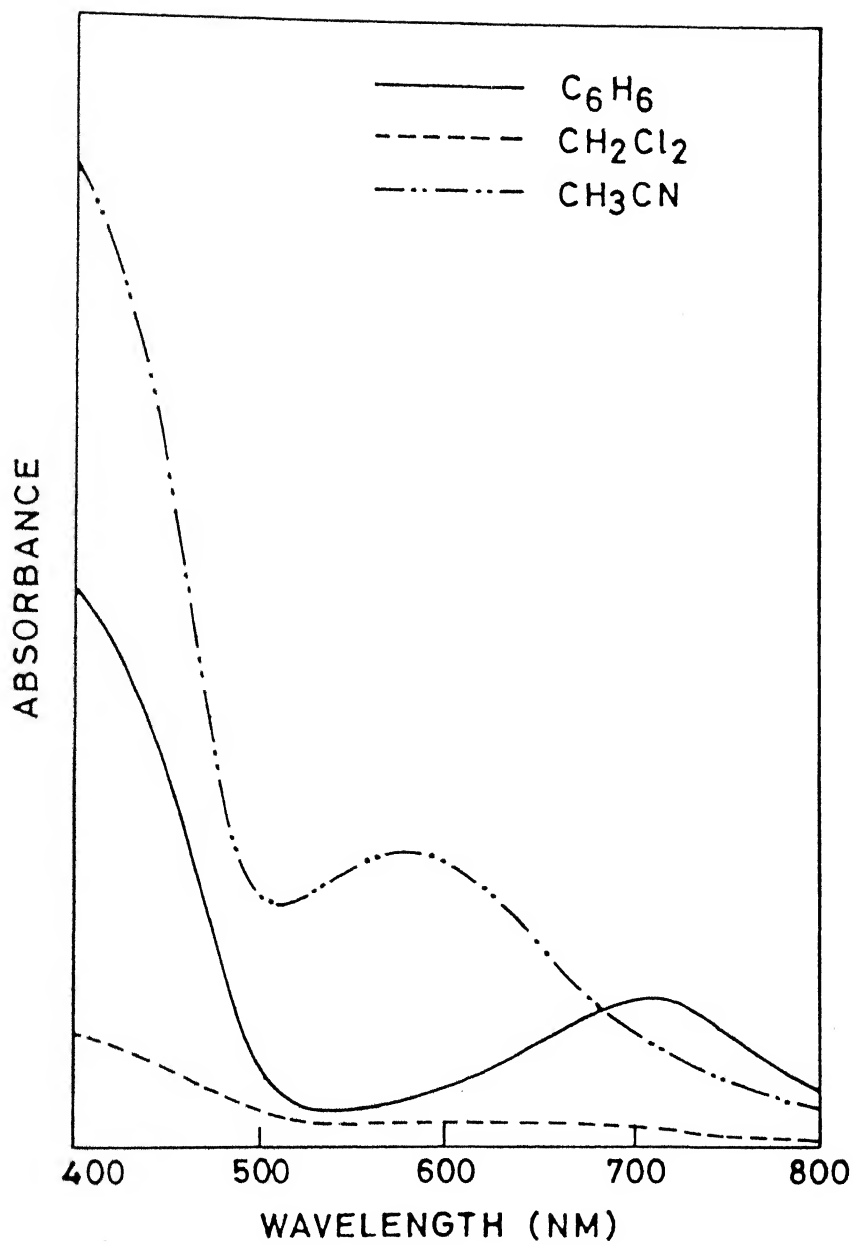
Fig.II.12 Absorption spectra of $[Mo(CO)_3Py]_2\text{-}\mu\text{-PBP}$.
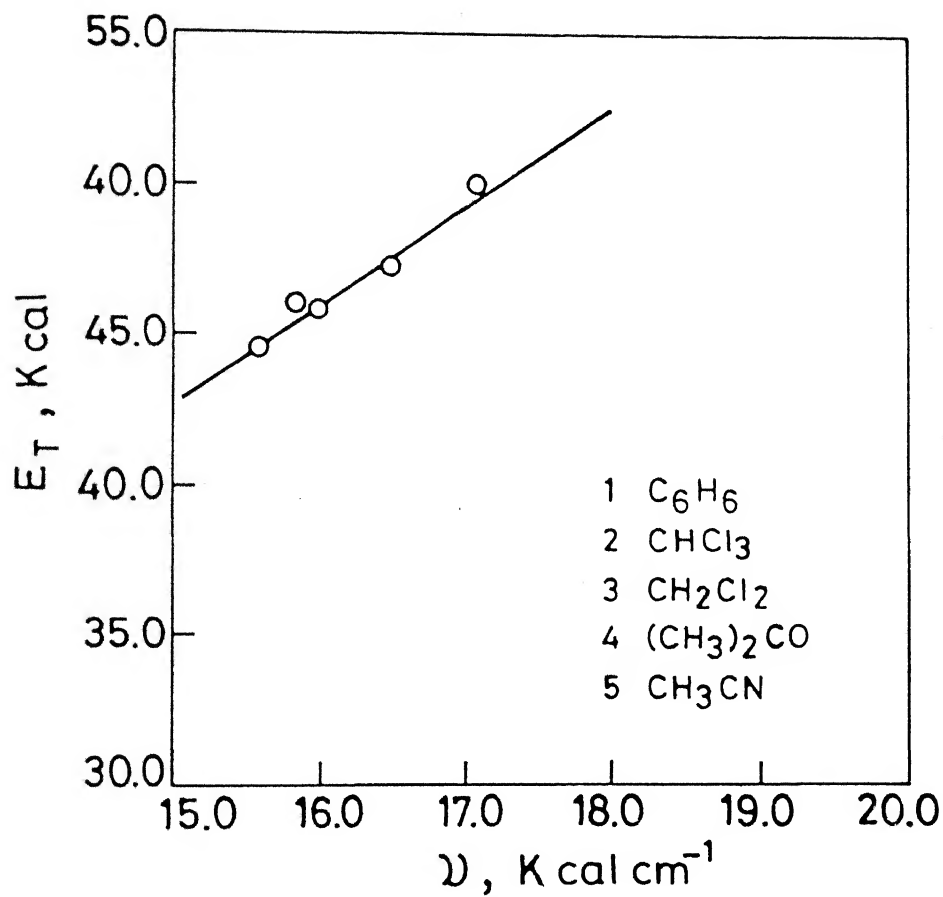
Fig.II.13 Plot of E_T vs $\nu_{(MLCT)}$ for $[Mo(CO)_3 PPh_3]_2 PBP$.
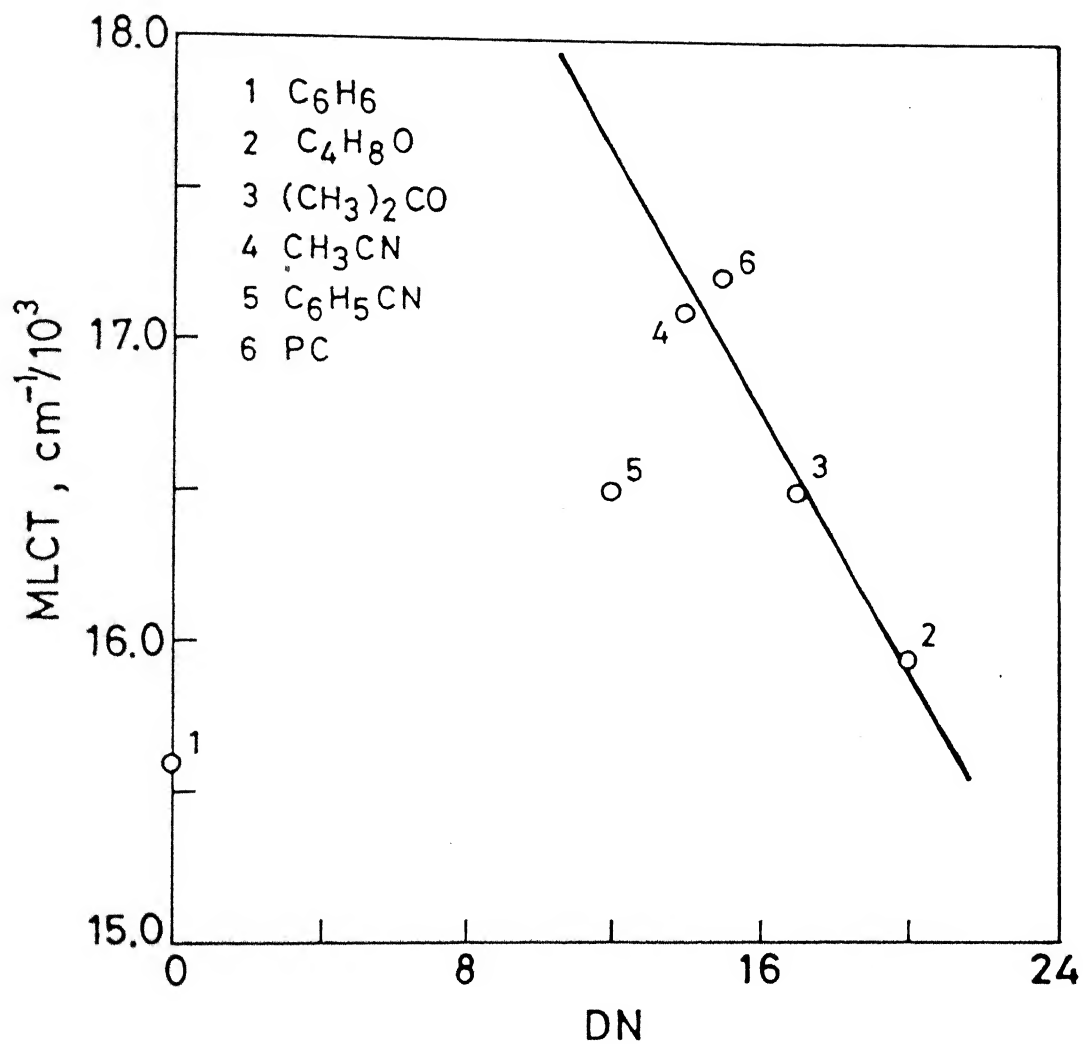
Fig.II.14   Plot of DN vs $\nu_{(MLCT)}$ for $[Mo(CO)_3 PPh_3]_2 PBP$.
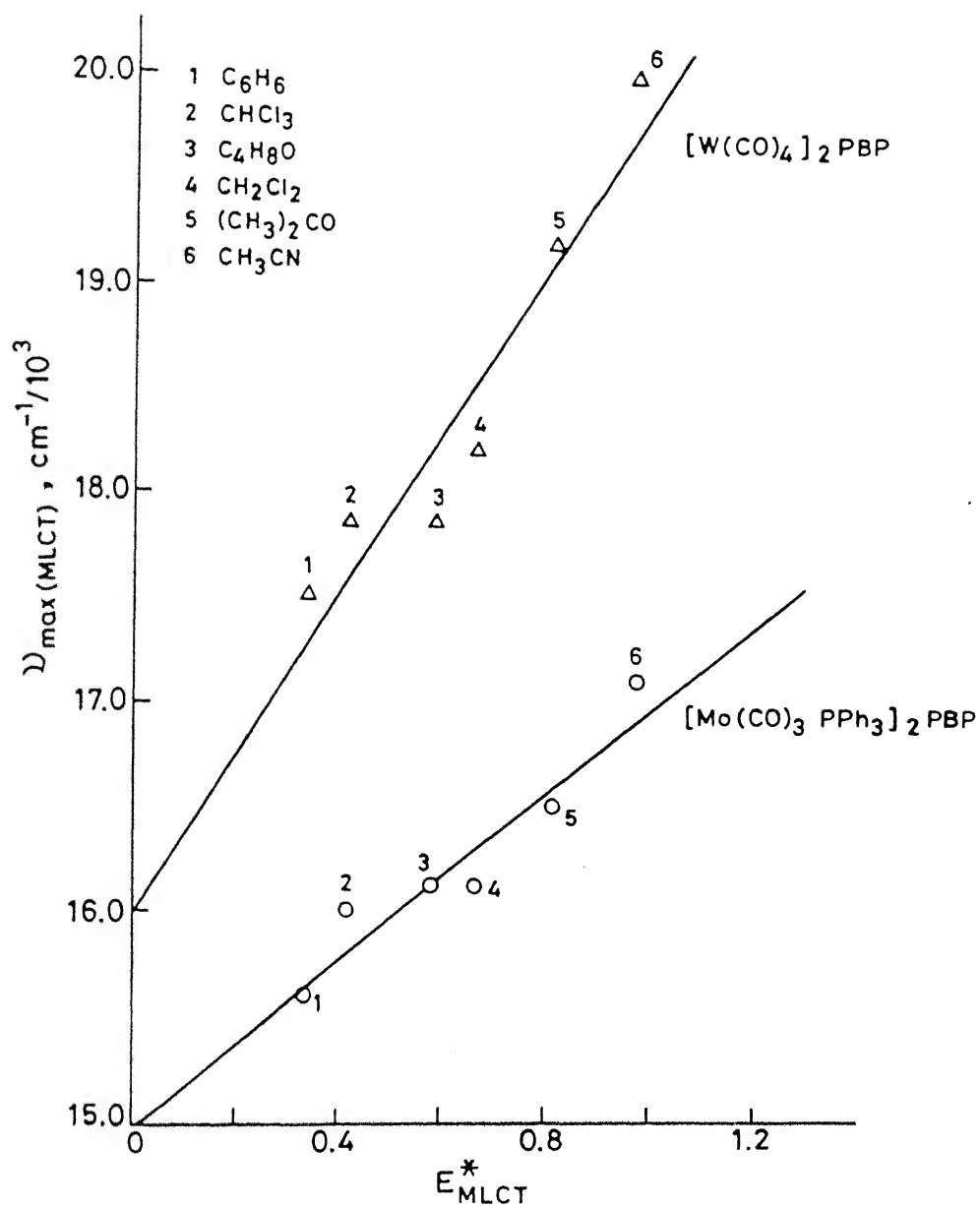
Fig.II.15 Plots of E^*_{MLCT} vs $\nu_{(MLCT)}$ for $[W(CO)_4]_2\text{-}\mu\text{-PBP}$ and $[Mo(CO)_3PPh_3]_2\text{-}\mu\text{-PBP}$.
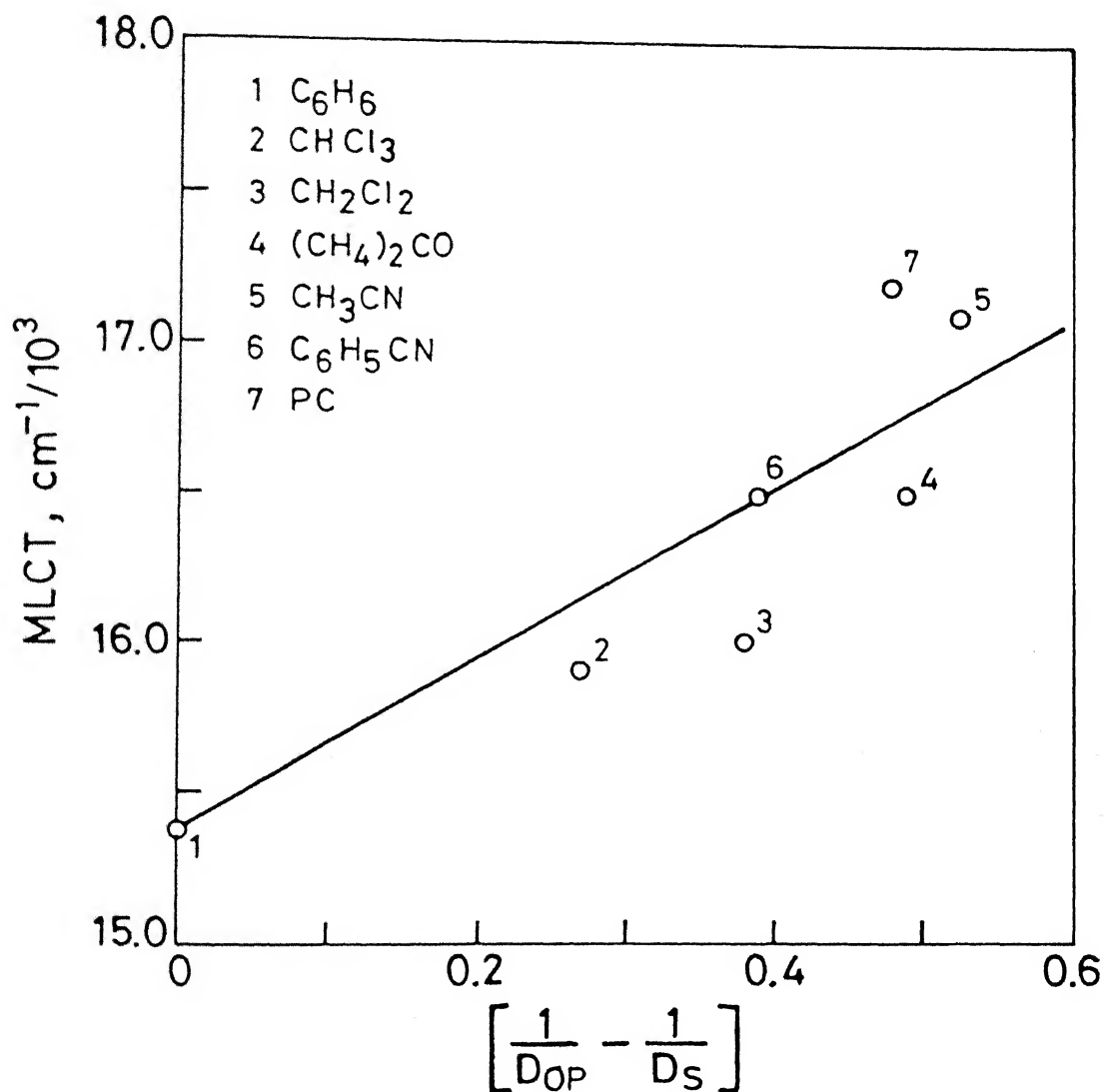
Fig.II.16 Plot of $(1/D_{op} - 1/D_s)$ vs $\nu_{(MLCT)}$ for
$[Mo(CO)_3PPh_3]_2-\mu-PBP$.
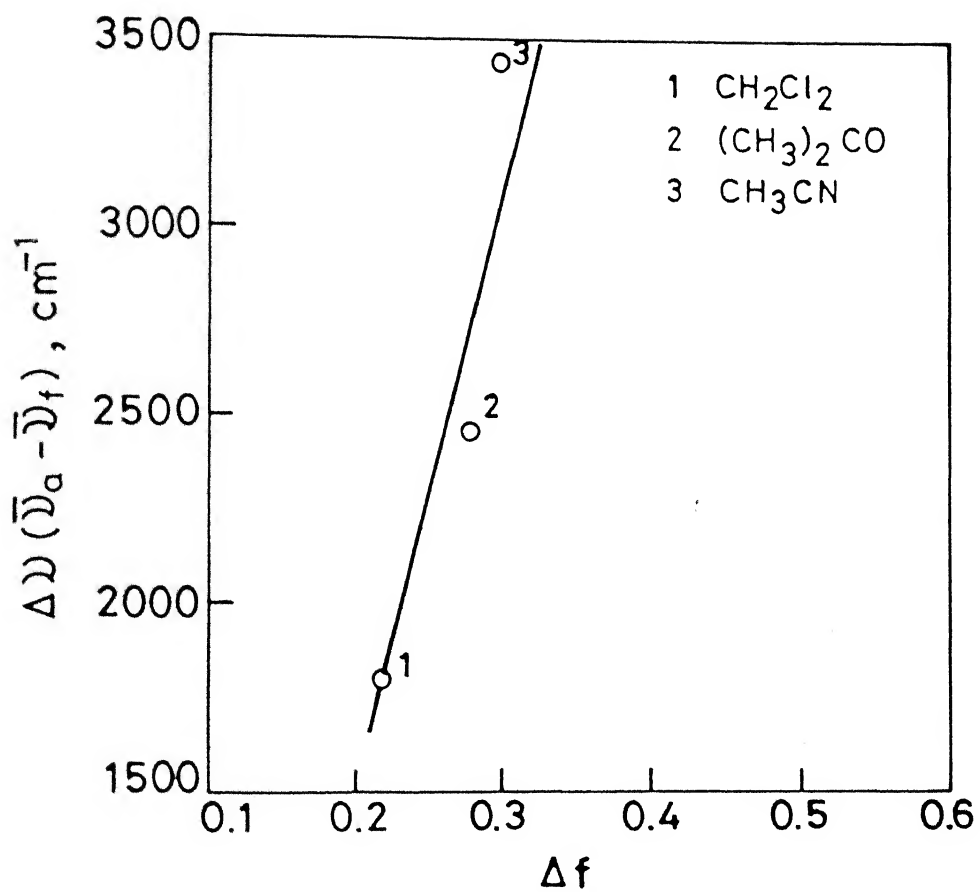
Fig.II.17 Plot of $(\bar{\nu}_a - \bar{\nu}_f)$ vs Δf for $[Mo(CO)_3 PPh_3]_2 - \mu - BBP$.
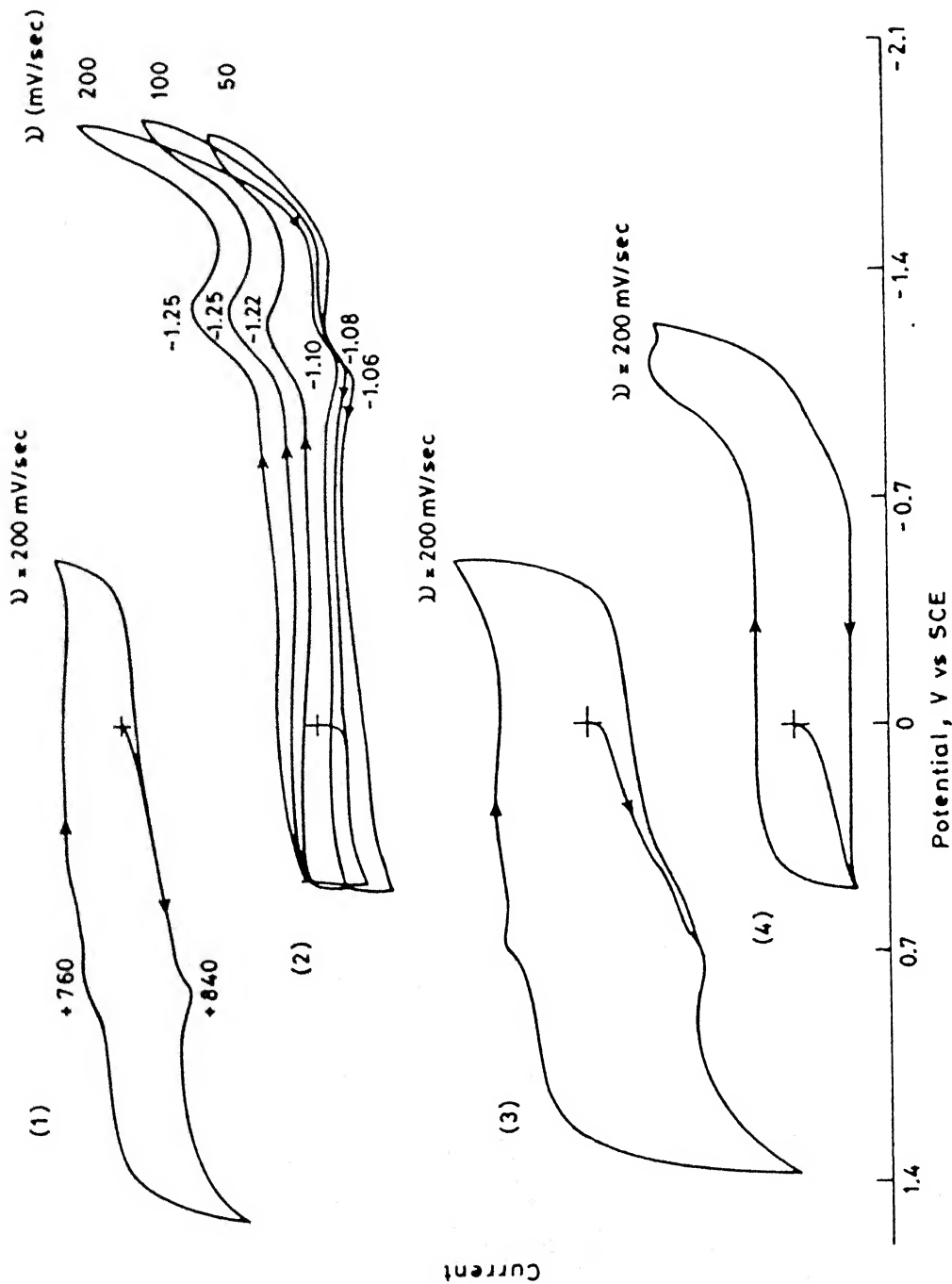
Fig. II.18 Cyclic voltammograms of (1) [W(CO)$_4$]$_2$BBP (oxidative scan) (Glassy carbon
electrode), (2) [W(CO)$_4$]$_2$BBP (reductive scan) (Glassy carbon electrode)
in varying scan rate: 50, 100 and 200, (3) [W(CO)$_3$PPh$_3$]$_2$PBP (oxidative
scan (pt. electrode), (4) [W(CO)$_3$PPh$_3$]$_2$PBP (reductive scan (pt. electrode)
in scan rate: 200 mVs^{-1}. Supporting electrolyte 0.1M TBAP.

Chapter – III

Reactivity of Trithiazyltrichloride towards
$[M(CO)_4(L-L)]$ $[M = Cr, Mo, W; L-L = bipy or$
$o-phen]$

Although trithiazyltrichloride besides S_4N_4 is one of the most versatile reagents for the syntheses of transition metal complexes containing unstable species like NS^+, S_2N_2, N_3S_2, $N_3S_2{}^{3-}$ $NSCl^{2-}$ as coligands, yet its behavior is highly unpredictable towards the nature of species it will yield under the given reaction conditions.[1-4] In continuation with our earlier efforts to examine the reactivity of trithiazyltrichloride with transition metal ions/complexes[5], this chapter reports the characterized products $[CrCl_3(L-L)]_2-\mu-S_2N_2$ and $[M(NSCl)Cl_3(L-L)]$ $[M = Mo,W;$ $L-L = bipyridine, o-phenanthroline]$ obtained by the reactions of trithiazyltrichloride towards the substituted Group 6 metal carbonyls.

III.1 Experimental Section

All reagents used were of AnalaR grade. The solvents were dried by known procedures and distilled prior to use. $[M(CO)_4(L-L)$ $[M = Cr, Mo, W; L-L = bipy, o-phen]$, $[M(CO)_3(L-L)Y]$ $[M = Mo, L-L $ bipy, o-phen; y-PPh_3, Py]$ and $(NSCl)_3$ have been prepared by liter ture methods.[6-8] Sephadex LH-20 has been purchased from Sigma Chemicals. All the reactions were carried out under pure and dry dinitrogen atmosphere.

(i) Reactions of Trithiazyltrichloride with $[Cr(CO)_4(L-L)]$
$[L-L = bipy, o-phen]$

A solution of trithiazyltrichloride (0.5 mmol) in 10 ml of dichloromethane was added with stirring to a solution of $[Cr(CO)_4$ $(L-L)]$ (.3 mmol) in dichloromethane (15 ml) whereby the evolution of a gas ensued. The stirring was continued until the gas evolut- ion had ceased. It took about an hour. A green insoluble compoun was formed in the reaction mixture. It was filtered and thoroughly washed with dichloromethane, methanol, ether and dried under vacuum. (Yield, ca 70%).

(ii) Reactions of Trithiazyltrichloride with $[Mo(CO)_4(L-L)]$
(L-L = bipy, o-phen)

A solution of $[Mo(CO)_4(L-L)]$ (.3 mmol) in dichloromethane (15 ml) was added with stirring to 10 ml of dichloromethane

solution of trithiazyltrichloride (.5 mmol). Immediately the
reaction started with the evolution of a gas. The stirring of
the reaction mixture was continued for about an hour till the
gas evolution ceased. During this time the color of the solution
changed to brown. It was filtered for any insoluble impurities
and the filtrate was concentrated to one fifth of its volume unde
reduced pressure. To the concentrate, light petroleum ether was
added in excess whereby a yellowish brown precipitate was formed.
It was separated by centrifugation, recrystallized with dichloro-
methane/petroleum ether, washed with petroleum ether and dried
under vacuum. The compound thus obtained was dissolved in 5 ml
of dichloromethane and was loaded on the top of the Sephadex LH-2(
column (25 x 2.5 cm). The compound was eluted with a mixture of
$CH_2Cl_2:CHCl_3$ (2:1, v/v). The brown band which was eluted first,
was concentrated to about 5 ml at reduced pressure from which the
compound was separated by precipitating it by adding excess of
light petroleum ether. (Yield, ca 40%).

(iii) Reactions of Trithiazyltrichloride with $[W(CO)_4(L-L)]$
      $[L-L = bipy, o-phen]$

The reaction was carried out by a procedure similar to that
reported in (ii) except that $[W(CO)_4(L-L)]$ was used in place of
$[Mo(CO)_4(L-L)]$ and the reaction was complete after 2 h. The color
of the compound obtained was dark brown. (Yield, ca 40%).

(iv) Reaction of Trithiazyltrichloride with $[M(CO)_3(L-L)Y]$

$[M = Mo \text{ or } W; \quad L-L = bipy, o-phen; \quad Y = PPh_3, Py]$

The reactions of $[M(CO)_3(L-L)Y]$ with trithiazyltrichloride have been carried out by the procedure similar to that described in (ii). Since $[M(CO)_3(L-L)Y]$ have a tendency to decompose in solution, $(NSCl)_3$ in dichloromethane was added immediately after the preparation of the solution of $[M(CO)_3(L-L)Y]$. However, the products obtained were highly unstable and became oily even before they could be properly dried.

The procedures for the Microanalytical, IR(KBr), electronic (CH_2Cl_2), NMR$(CDCl_3)$ and ESR$(CH_2Cl_2$ and powder) measurements have been described earlier.[10] The reflectance spectra of the chromium compounds were obtained on a Hitachi model spectrophotometer. The magnetic susceptibility of the compounds were measured on a Guoy's balance using $Hg[Co(NCS)_4]$ as standard. The results are given in Table III.1.

III.2 Results and Discussion

The microanalytical data of the various compounds obtained as a result of the reactions of trithiazyltrichloride with the substituted group 6 metal carbonyls are given in Table III.1. The data correspond very well with the formulations $[CrCl_3(L-L)]_2\text{-}\mu\text{-}S_2N_2$ and $[M(NSCl)Cl_3(L-L)]$ $[M = Mo, W; (L-L) = bipy, o-phen]$.

A few of the starting materials like $[Mo(CO)_3(L-L)Y]$ $[L-L = bipy, o-phen, Y=PPh_3, Py]$ decompose in solution during the reaction liberating possibly a molecule of triphenylphosphine or pyridine. Furthermore, the products obtained as a result of these reactions were also unstable and had a tendency to become oil even at low temperatures. We believe that $(NSCl)_3$ reacted independently with the dissociated triphenylphosphine or pyridine yielding polymeric products containing PPh_3, nitrogen and/or sulfur. Unfortunately, all our attempts to purify the products were unsuccessful. These were found to be contaminated with a number of impurities and could not be characterized. They have not been listed in Table III.1.

The chromium complexes were insoluble in almost all common organic solvents. The molybdenum and the tungsten compounds were however soluble in some common organic solvents. The latter were unstable at room temperature and changed their colors to red. However, they could be preserved at low temperatures in sealed tubes.

These reactions exhibited the oxidizing properties of $(NSCl)_3$. Chromium, molybdenum and tungsten got oxidized from zero to their stable oxidation states +3 (Cr) and +5 (Mo, W). Although $(NSCl)_3$ has a potential of oxidizing molybdenum and tungsten to +5 oxidation states, but it could oxidize chromium to +3 state only because of a large amount of energy needed to

go to higher states. This is expected because of the large amount

of energy needed to oxidize chromium to oxidation state higher

than +3. Furthermore, +3 is the most stable oxidation state of

chromium while the molybdenum and tungsten in oxidation states

lower than +5 and +6 are usually unstable and get disproportionated

except when there is either metal-metal bond or they have CO as

ligand.

III.3a IR Spectra

The infrared spectra of chromium complexes displayed,
besides the characteristic bands of the ligands (bipyridine and
o-phenanthroline), bands around 860 cm^{-1} (strong), 470 cm^{-1}
(medium) and around 360 (shoulder), 350 (medium) and 330 (shoul-
der) cm^{-1}. The coordinated cyclo S_2N_2 group consistently exhibits
two bands at 860 cm^{-1} (s) and 470 cm^{-1} (m) arising due to the
B_{3u} and deformation modes of S_2N_2 ring respectively (Fig.III.1)[9,10].
The positions of these absorption bands remain practically constant
in all the S_2N_2 complexes. Consequently, the bands at 860 cm^{-1}
and 470 cm^{-1} are assigned to the characteristic vibrations of
bridging S_2N_2 group.[9,10] In addition, the shift of 65 cm^{-1} towards
lower wave numbers from that of the free S_2N_2 reflects the coordi-
nated nature of S_2N_2 moiety. The three vibrations around 350 cm^{-1}
which do not appear in the other bipyridine or o-phenanthroline
complexes have been assigned to $\nu_{(Cr-Cl)}$. The positions of these
bands corroborate well with those of other earlier studied chromium

compounds having bridging S_2N_2 and Cr-Cl bonds.[9,10] In the spectrum of o-phenanthroline complex, the band at 860 cm^{-1} was masked by the highly intense o-phenanthroline band in this region.

Molybdenum and tungsten complexes compared to those of chromium ones exhibited entirely different behavior which is not surprising because of the difference in the chemistry of chromium from that of molybdenum and tungsten. Their infrared spectra exhibited intense bands around 950 cm^{-1} and 500 cm^{-1} assigned to $\nu_{M=N=S}$ and ν_{S-Cl} respectively (Fig. III.2).[11-15] Spectroscopic and single crystal X-ray studies of the NSCl-transition metal complexes describe the bonding in $\left[M-(NSCl)^{2-}\right]$ unit in terms of resonance structures M=N=S⟍Cl and M-N≡S⟍Cl with the dominance of the former one.[4] Similar mode of bonding is therefore suggested in the molybdenum and tungsten complexes described herein. It has been further corroborated by the formation of the nitrido complexes as a result of thermolysis.[11-15] ν_{M-Cl} bands appeared around 320 cm^{-1}.

III.2b Electronic Spectra

Chromium complexes exhibited electronic spectra which are typical of Cr(III) complexes (Fig. III.3).[16,17] It exhibited peaks at 17,250 cm^{-1} and 28,500 cm^{-1} with a number of shoulders around the second band. Generally the $^4A_{2g} \longrightarrow {}^4T_{2g}$ transition in the spectra has been assigned around 17,000 cm^{-1}. The assignments have been carried out assuming the octahedral symmetry

though the molecular microsymmetry is significantly lower (C_{3v}). Splitting due to lower symmetry is observed in 17,000 cm^{-1} band. The extent of trigonal distortion from the octahedral field in terms of v/2 (1140 cm^{-1})[17] and the value of 10 Dq have been evaluated from the band around 17,000 cm^{-1} (term distance v/2 between ^4E and ^4A states obtained by splitting of $^4T_{2g}$ level because of the descend in symmetry).

The assignment of the second d-d transition is a little controversial which is largely due to the difficulty in resolving the absorption band from charge transfer transitions in that region. However, the position of this transition is expected to be <u>ca</u> 7000 cm^{-1} higher than that of the first band.[18] It should therefore, appear around 24000 cm^{-1}. A broad and intense band exhibiting fine structure is observed at 28,500 cm^{-1} with shoulders at 22,220 cm^{-1}, 23,529 cm^{-1}, 25,640 cm^{-1}, 33,000 cm^{-1} and 34,000 cm^{-1}. Among the shoulder bands, the one at 23,529 cm^{-1} is the weakest one. It is therefore assumed that the $^4T_{1g}(F) \longleftarrow {}^4A_{2g}$ band appeared as a shoulder at 23,529 cm^{-1}. The bands at 25,640 cm^{-1}, 28,500 cm^{-1} and 34,000 cm^{-1} are the charge transfer and/or intraligand bands of bipyridine or o-phenanthroline.

Besides the aforesaid bands, the spectra also exhibited two narrow spin forbidden (quartet-doublet) transitions (Ruby lines) at 15,400 and 14,300 cm^{-1}. These may arise due to spin flip within t_{2g} set of chromium and could be assigned to $^2E_g \longleftarrow {}^4A_{2g}$ and

$^2T_{1g} \longleftarrow {}^4A_{2g}$ transitions. Though these should be degenerate in the perfect octahedral symmetry, but this does not hold true when spin orbit forces and lower crystalline field are considered. However there is a possibility of both the bands to be due to $^2E_g \longleftarrow {}^4A_{2g}$ transitions which has been split because of the lowering of symmetry from O_h to C_{3v}. But the literature data suggest that the observed energy difference between the two bands is a little too high for assigning them to the latter transitions. The first alternative is therefore preferred for their assignments. The energy ordering of ^2E_g and $^2T_{1g}$ states in the complexes has been assumed on intensity considerations. According to Ballhausen ^2E_g band should be about 8/3 times more intense compared to $^2T_{1g}$ one. The experimental ratio of the intensities of the bands at 15,400 cm^{-1} and 14,300 cm^{-1} is about 8/3. This indicates that the 15,400 cm^{-1} band should arise from $^2E_g \longleftarrow {}^4A_{2g}$ transition and the one, at 14,300 cm^{-1}, from $^2T_{1g} \longleftarrow {}^4A_{2g}$ transition.

The values of 10 Dq, B_{35}, B_{55}, β_{35}, β_{55}, and the splitting parameter v of $^4T_{2g}$ level have been evaluated from the positions of the aforesaid bands. The standard equations[20] have been used for calculation including configuration interaction (Table III.1). The results show that the value of β_{55} is considerably less than unity. This indicates significant π-type interaction of the metal electrons with the π^* orbitals of the bipyridine or phenanthroline ligand. The value of β_{35} which was evaluated from the ligand field transition, $^4T_{1g} \longleftarrow {}^4A_{2g}$, suggests the extent of

repulsion within both σ and π bonding subsets (t_{2g}^3, $t_{2g}^2 e_g^1$). Thus the difference between β_{35} and β_{55} values can be assumed to be related to the degree of σ interaction arising from the covalent overlap of the metal and ligand orbitals. However the values of β_{35} and β_{55} lower than one suggest the importance of both σ-covalency and π-back bonding in the chromium complexes.

The electronic spectra of the molybdenum and tungsten compounds exhibited no sharp bands in the visible region. A weak shoulder appeared at around 22,500 cm^{-1} respectively, which has been assigned to $^2B_1 \longleftarrow {}^2B_2$ transition as expected for a d^1 system.[21] The axial distortion (<u>vide supra</u>) and hence the reduction of the symmetry from the octahedral should give rise to another component assignable to $^2E_1 \longleftarrow {}^2B_2$ transition. This could not be observed due to the weak intensities of the bands. The spectra showed strong bands in the uv-region, assignable to $\pi(X) \longrightarrow d\pi(M)$ charge transfer[22] transitions and intraligand bands of bipyridine/ o-phenanthroline.

III.2c Magnetic Properties

The effective magnetic moment (3.80 B.M.) for chromium compound suggested +3 oxidation state of the metal. The ground term for Cr^{3+} is $^4A_{2g}$ and therefore one does not expect any orbital contribution to the magnetic moment of Cr(III). However the magnetic moment is reduced below the spin-only value (3.87 B.M.) because of the (1-4 λ/10 Dq) effect.[23] Using the literature

equations[23] (including TIP component) and the experimental value of μ_{eff} the approximate values of the reduction factor, k, has been evaluated. Its value lower than one (Table III.1) suggests sufficient delocalization of the ligand electrons onto metal t_{2g} orbitals in forming molecular orbitals due to which spin orbit coupling constant is reduced to ($= \lambda_o k$). The delocalization of the d electrons have also been indicated by the results of the electronic spectra of these compounds (vide infra).

The effective magnetic moments of molybdenum and tungsten complexes are given in Table III.1. These are nearing the spin only magnetic moment values. However, in an octahedral field using the free ion spin orbit coupling constant for molybdenum and tungsten, one expects molybdenum(V) ion to have a room temperature magnetic moment of about .9 B.M. and tungsten, a value of about .5 B.M. The observed magnetic moment values therefore strongly suggest the reduction in the spin-orbit coupling constant and in the symmetry of the ligand fields. These have been evaluated and the values of k are given in Table III.1 suggesting a large delocalization of the electrons in the complexes. These two factors considered together account for the observed magnetic moment values.

III.2d E S R Spectra

The powder ESR spectra of the chromium complexes showed a broad band with an isotropic 'g' value. This suggests a short

relaxation time by some mechanism causing the broadening of the ESR signal. However, the anisotropy in the g value could not be resolved even by taking the spectra at 77K.

The solution ESR spectra of the Mo(V) compounds are characteristic of d^1 mononuclear molybdenum having a strong central line and six hyperfine structures due to $^{95,97}Mo$ (I = 5/2). In bipyridine complex, two of the hyperfine lines seem to be embedded in the central line and this was checked by simulating the spectra using the computer programme described elsewhere[24] (Fig. III.4). The powder and frozen glass ESR spectra did not reveal any anisotropy, instead a broad band was observed. The loss of aniso-tropy in the g value is believed to result from the exchange inter-action between the number of molybdenum atoms due to undiluted sample giving a total spin greater than S=1/2. In the absence of any zero field splitting all the transitions between the neighbor-ing Ms states will occur at the same field giving a single absorp-tion line.[25]

The solution ESR spectra of the tungsten compounds exhibited a strong central line with no hyperfine structures (Fig. III.5). The powder and the frozen glass spectra also did not reveal any anisotropy in g value.

The molecular weights of the molybdenum and tungsten com-pounds were also determined by the F.D. mass spectra of the compounds (cf. Table III.1). These corresponded well with the theoretical values.

The foregoing results and discussion reveal that $[Cr(CO)_4(L-$ react with $(NSCl)_3$ yielding insoluble complexes having the formula $[CrCl_3(L-L)]_2-\mu-S_2N_2$ in which S_2N_2 form a bridge between the two $[CrCl_3(L-L)]$ moieties. Unfortunately, because of the highly insoluble nature of the complexes, we are unable to decide if the latter moiety is ionic or neutral. In case they are neutral, a dimeric structure with S_2N_2 bridge is proposed. In the evantualit[y] of their being cationic, a tetrameric structure (similar to Dehnicke's complex)[10] or a polymeric structure with chloro and S_2N_2 bridges is proposed. The complexes of molybdenum and tungsten appear to be monomeric having the structure similar to that of $[MCl_4(NSCl)]_2$ (Dehnicke's complex)[12,13] in which two of the Cl^- ions have been substituted by (L-L) ligands. The data also suggested that there is a large degree of delocalization of d electrons and covalency in the bonds. Furthermore, a departure from the perfect O_h symmetry is exhibited in these complexes.

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   b. The simulation was basedon a spin Hamiltonian of the form

$$\mathcal{H}_s = \beta_e \cdot H \cdot g \cdot S + I \cdot A \cdot S + I \cdot Q \cdot I - g_n \cdot \beta_n \cdot I \cdot H$$

where all the symbols have their usual meaning. The resonance peak position calculated by above equation are convoluted with a Gaussian line shape function with a peak to peak derivative line width appropriate to the spectrum being simulated.

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Table III.1 Microanalytical and spectral (IR, UV-VIS, ESR) and magnetic data of the compounds.

Sl. No.	Compound[1] (Mol.wt.)	Analysis in % Exptl./(calc)						Characteristic IR bands (in cm^{-1})	Characteristic UV-VIS (kK) spectral bands	10 Dq cm^{-1}	B_{35} (cm^{-1}) $(\beta_{35})^2$	B_{55} (cm^{-1}) $(\beta_{55})^2$	ε^3	μ_{eff}(RT) B.M ($\langle g \rangle$)
		C	H	N	S	Cl	M							
1.	[CrCl$_3$bipy]$_2$ μ-S$_2$N$_2$ G	33.6 (33.2)	1.8 (2.2)	11.5 (11.7)	8.4 (8.9)	29.9 (29.6)	14.2 (14.5)	860(s),470(m), 360(sh),350(m), 330(sh)	34.0,33.0(s), 25.6(s),23.5(w), 22.2(sh),28.5(br), 17.2(m),16.1(sh), 15.4(s),14.3(s)	16,500	713.6 (.77)	833 (.9)	.14	3.80 (1.987)
2.	[CrCl$_3$ophen]$_2$ μ-S$_2$N$_2$ G	37.8 (37.4)	1.9 (2.1)	10.7 (11.0)	8.1 (8.4)	28.0 (27.8)	13.0 (13.5)	860(s),470(m), 360(sh),350(m), 330(sh)	34.0,33.0(s), 25.6(s),23.5(w), 22.2(sh),28.5(br), 17.2(m),16.1(sh), 15.3(s),14.3(s)	16,510	705.9 (.767)	825 (.897)	.14	3.81 (1.985)
3.	[Mo(NSCl)Cl$_3$bipy] YB (443)	27.3 (27.1)	1.6 (1.8)	9.8 (9.5)	7.5 (7.2)	32.2 (32.1)	20.9 (21.7)	970(m),940(m), 920(m),500(m), 340(s),320(sh)	22.1(w)	22,110				1.68 (1.950)
4.	[Mo(NSCl)Cl$_3$ophen] YB (462)	32.2 (30.9)	1.8 (1.7)	8.9 (9.0)	6.5 (6.8)	30.8 (30.4)	19.9 (20.6)	970(m),940(m), 920(m),500(m), 340(s),320(sh)	22.1(w)	22,110				1.68 (1.951)
5.	[W(NSCl)Cl$_3$bipy] B (526)	22.4 (22.6)	1.7 (1.5)	8.2 (7.9)	5.8 (6.0)	26.4 (26.8)	33.6 (34.7)	990(s),950(m), 920(m),498(s), 360(s),330(sh)	23.5(w)	23,529				1.55 (1.946)
6.	[W(NSCl)Cl$_3$ophen] B (551)	25.8 (26.0)	1.6 (1.4)	7.2 (7.6)	5.3 (5.2)	25.1 (25.6)	32.8 (33.2)	990(s),950(m), 920(s),495(s), 360(s),335(sh)	23.5(w)	23,529				1.55 (1.946)

1. Colour: G=Green; YB=Yellowish Brown; B=Brown; 2. $\beta = \dfrac{B}{B_o}$, $B_o = 920$ cm^{-1} for free ion; 3. $\varepsilon = 1 - \dfrac{\beta_{35}}{\beta_{55}}$.

Fig.III.1 Infrared spectra of $[CrCl_3(bipy)]_2-\mu-S_2N_2$.
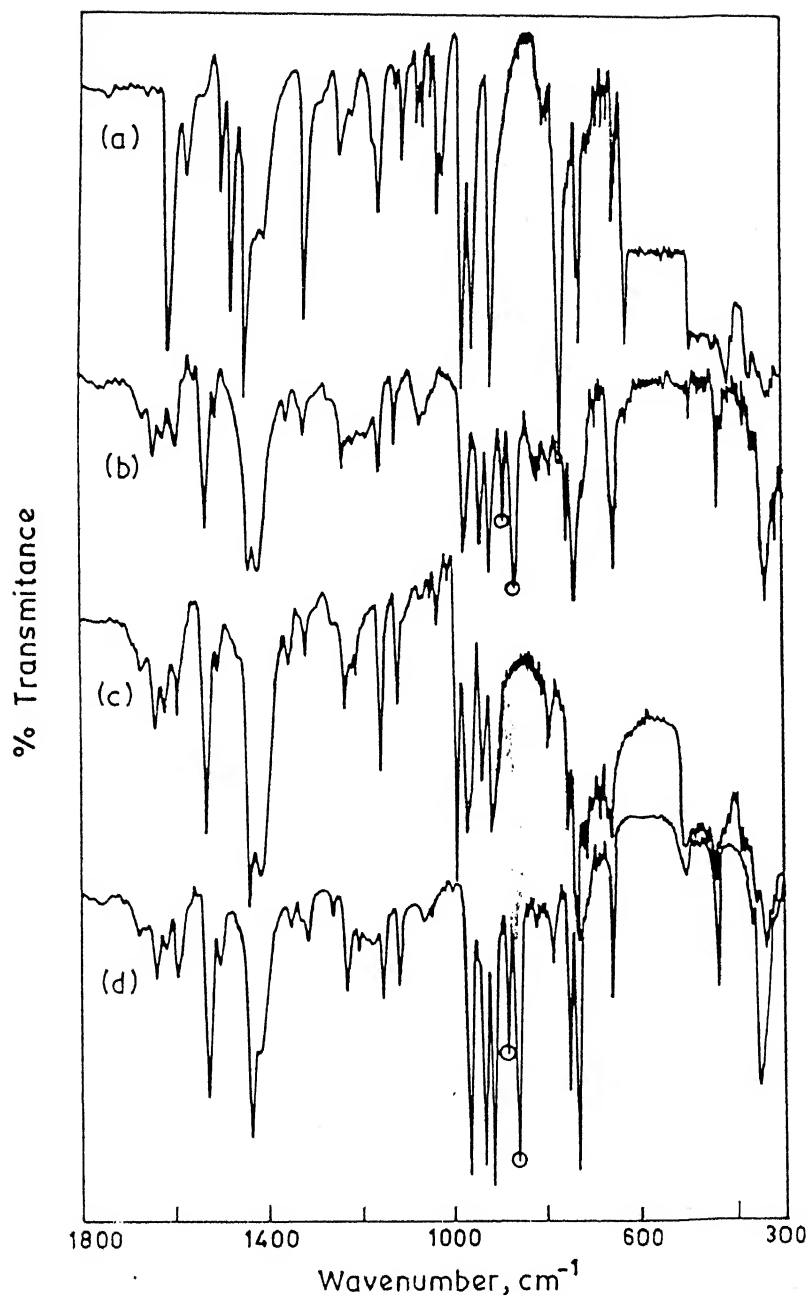
Fig.III.2 Infrared spectra of [Mo(NSCl)Cl₃bipy] (a),
[Mo(NSCl)Cl₃(o-phen)] (b), [W(NSCl)Cl₃bipy] (c),
[W(NSCl)Cl₃(o-phen)] (d).
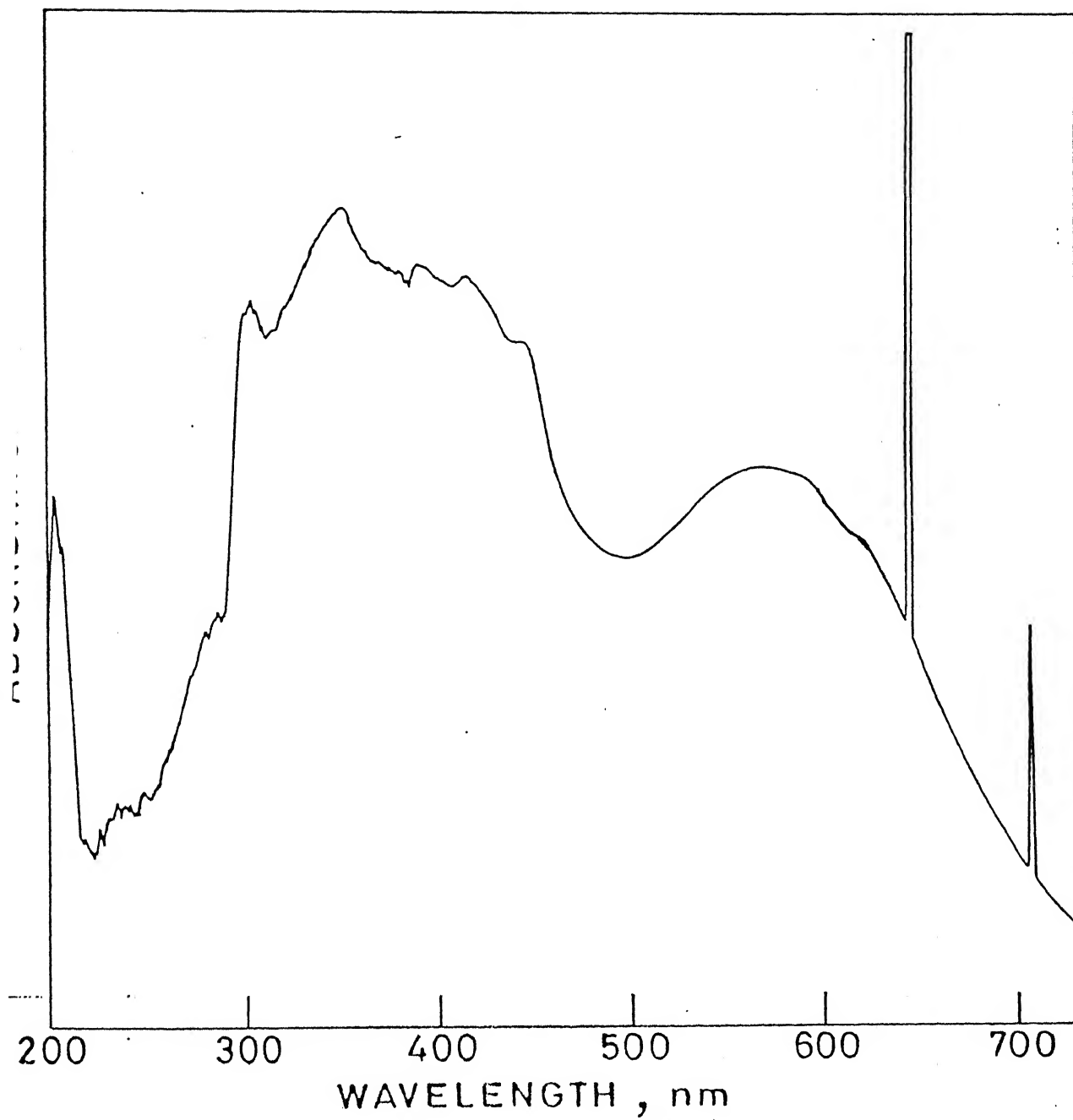
Fig.III.3   Electronic spectra of $[CrCl_3(bipy)]_2$-μ-S_2N_2.

(i)

(ii)

MAGNETIC FIELD (gauss)
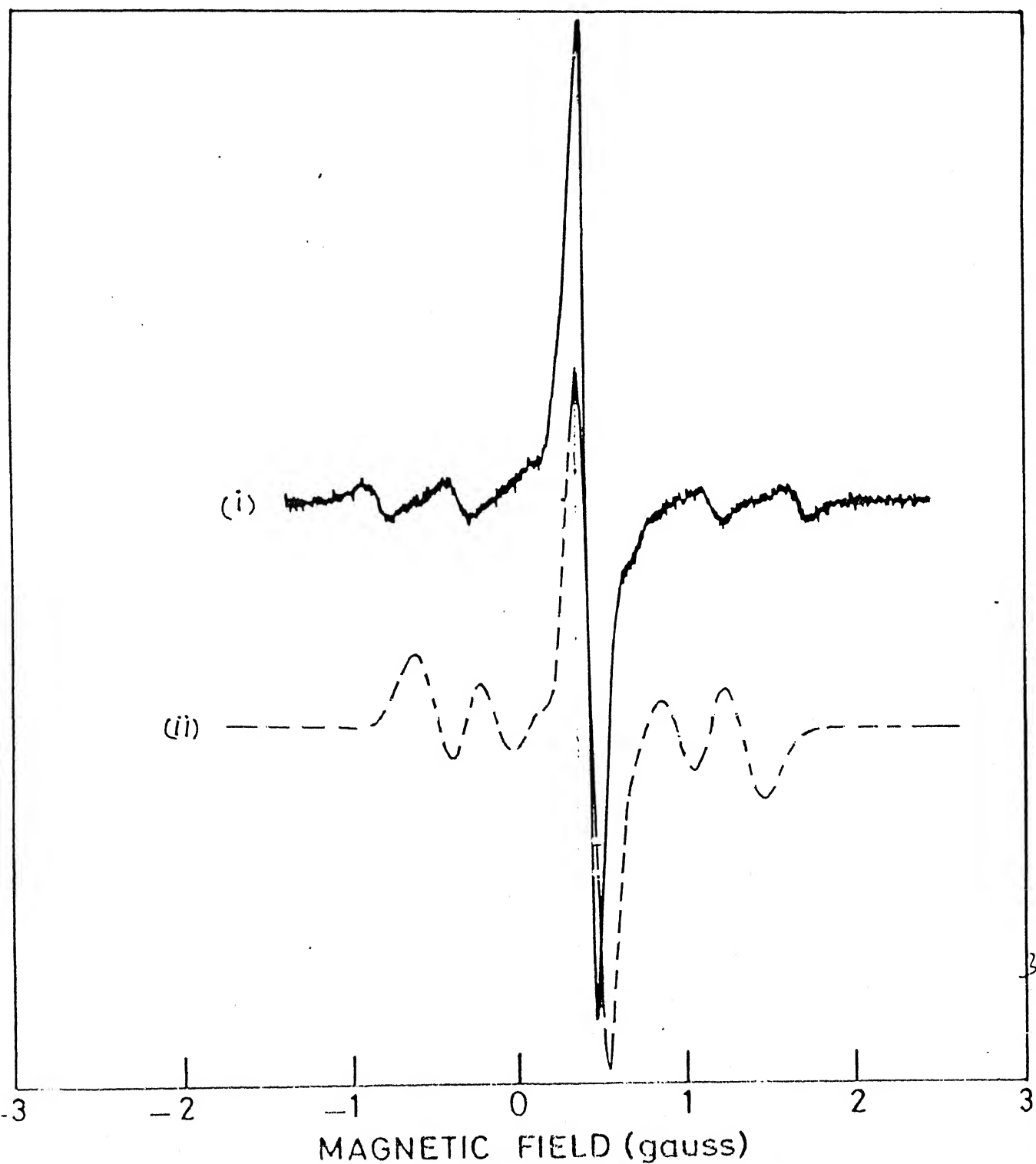
Fig.III.4   ESR spectra of $[Mo(NSCl)Cl_3(bipy)]$ in CH_2Cl_2 solution at 300K.   Experimental (————————) Simulated (——————————).
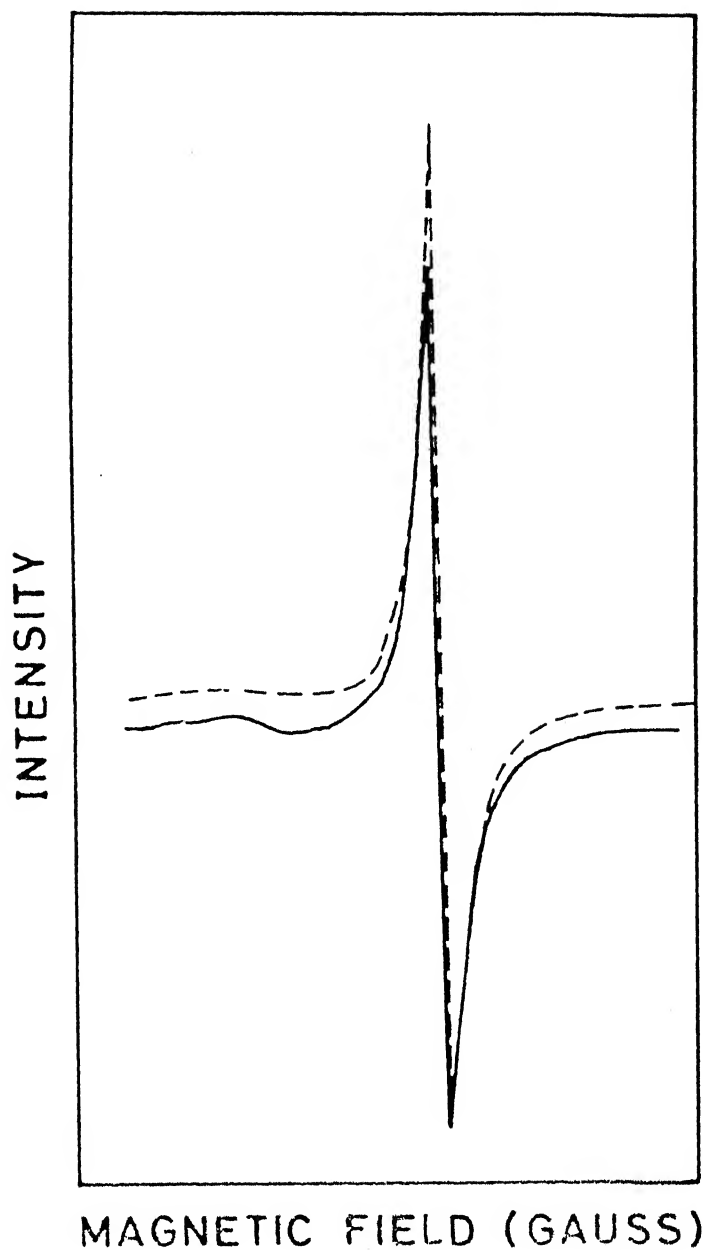
Fig.III.5 ESR spectra of $[W(NSCl)Cl_3(bipy)]$ in CH_2Cl_2

solution at 300K. Experimental (————————)

Simulated (—————————).

Chapter - IV

Chlorothionitrene Complexes of Molybdenum and Tungsten

        Our efforts in the recent years have been in a direction to search the possibility of using trithiazyltrichloride as a thionitrosylating agent for the synthesis of thionitrosyls, a field which is still in an embryonic state. While making these efforts, the reactions of trithiazyltrichloride with substituted M(II) (M = Mo, W) carbonyl complexes having 2,2'-bipyridine or 1,10-phenanthroline as coligand afforded complexes in which NSCl is bonded to M(VI) (M = Mo, W) in the form of chlorothionitrene group M=N=S$\diagdown_{Cl}$, a bonding mode which has been fairly studied. This chapter focusses on the detailed synthesis and characterization of these compounds.

IV.1 Experimental Section

All the chemicals used were of reagent or AnalaR grade. $Mo(CO)_6$, $W(CO)_6$, $MoCl_5$, WCl_6, 2,2'-bipyridine and 1,10-phenanthroline were purchased from Aldrich Chemical Company and were used as such. Sephadex LH-20 was procured from Sigma Chemical Company. $[M(CO)_3(L-L)X_2]$ (M = Mo, W; (L-L) = bipy or o-phen; X = Br, I)[1], $[M(NSCl)Cl_4]_2$[2,3] (M = Mo, W) and trithiazyltrichloride[4] were prepared by literature methods. Solvents were purified and dried by standard methods[5] and degassed prior to use. All experiments were performed under nitrogen atmosphere.

Physical and Spectral measurements

General information concerning instrumentation and analyses of the complexes is described in chapter II. ESR spectra in dichloromethane at room and liquid N_2 temperature and X-ray powder patterns of the complexes were recorded using century series E line ESR spectrometer and 150-Debyeflex 2002 diffractometer respectively.

Preparations

(A) Reaction Medium Dichloromethane

(i) Reaction of Trithiazyltrichloride with $[M(CO)_3(L-L)X_2]$
(M = Mo, W; (L-L)=bipy, o-phen; X = Br, I)

A solution of $(NSCl)_3$ (<u>ca</u> 0.03 mmol) in 10 ml of

dichloromethane was added to a stirred solution of $[M(CO)_3(L-L)X_2]$ (ca. 0.1 mmol) in 15 ml of dichloromethane. After the mixture was stirred for approximately 1 h and gas evolution had ceased, the resulting solution was concentrated under reduced pressure to about 5 ml. The product (I) was precipitated from the concentrate with light petroleum ether, which was filtered and washed with a little of benzene and then with copios amounts of petroleum ether. The product was recrystallized from dichloromethane/petroleum ether. The recrystallized product was further purified by column chromatography using Sephadex LH-20 column (25 cm x 2.5 cm) and 1:1 mixture of dichloromethane and chloroform as eluent (elution rate, approximately 1-2 ml min^{-1}). A broad brown band formed on the column top was eluted by CH_2Cl_2 and the eluent was concentrated under reduced pressure to about 5 ml and kept at 0°C for a few days for crystallization. Thereby microcrystals (II) were deposited on the sides of the flask. These were collected, washed with a little benzene, petroleum ether and dried in vacuum. The same compound was also obtained by precipitating it from the concentrated eluent with light petroleum ether and drying it under vacuum (yield, 50%). The compounds I and II were found to be identical as has been found from their chemical analyses, m.p., mixed m.p., IR and UV-visible spectral data. The compound has the formulation $[M(NSCl)Cl_3X'(L-L)]$ (M = Mo, W; X'= Cl or Br).

(ii) Reactions of 2,2'-bipyridine and 1,10-phenanthroline with $[M(NSCl)Cl_4]_2$ (M = Mo, W)

A stoichiometric amount of bipy or o-phen was added to a stirred suspension of $[M(NSCl)Cl_4]_2$ (ca. 0.1 mmol) in 25 ml of dichloromethane and stirring was continued for 1 h when the solution attained brown color. It was filtered and the filtrate was concentrated under reduced pressure. The concentrate was processed as described in A(a) (yield ∼60%).

(B) Reaction Medium Tetrahydrofuran

The reactions were carried out by the same procedure as described in A(i) and A(ii) except that tetrahydrofuran was used as the reaction medium in place of dichloromethane. The working up of the reaction product, recrystallization of the compounds and their purification by column chromatography were done as described in (A) (In THF, compounds became oily during recrystallization process).

(C) Thermolysis of $[M(NSCl)Cl_3X'(L-L)]$ (M = Mo, W; L-L = bipy or o-phen; X' = Cl, Br)

Thermolysis of $[M(NSCl)Cl_3X'(L-L)]$ (exactly weighed) was carried out at about 250°C for 4 h in a two necked flask having an inlet and outlet tube. Through the inlet tube a slow stream

of nitrogen gas was allowed to pass slowly, while the gaseous
products coming out of the outlet tube were bubbled into water.
The hydrolyzed products were then analyzed for sulfur and chloride
ion. The compound after thermolysis changed to marroon(M=Mo) or
pinkish grey (M=W) and was analyzed as $[MNCl_2X'(L-L)]_n$ (III).

In another experiment, the known weight of $[M(NSCl)Cl_3X'-(L-L)]$ was heated at $250^{\circ}C$ for 4 h over a watch glass. After
cooling, the change in weight was recorded. The loss in weight
of the complex corresponded approximately to one mole of SCl_2 per
mole of the complex.

IV.2 Results and Discussion

The reactions of trithiazyltrichloride with $[M(CO)_3X_2(L-L)]$
yielded the novel compounds of empirical formula $[M(NSCl)Cl_3X'-(L-L)]$ (I) (cf. Table IV.1). Apart from being a ligand linked to
the metal ion as $NSCl^{-2}$, trithiazyltrichloride oxidizes the metal
from +2 to +6 oxidation state. In iodo complexes, both the
iodide ions and in bromo ones only bromide ion were substituted
by the chloride ions in their respective products. The approxi-
mate amount of librated iodine during the reaction was iodometri-
cally estimated which conformed to two moles of iodide ions per
mole of the complex.

The compounds are soluble in halo-substituted solvents and
decompose in methanol to yield a polymeric nitrido compound of

emperical formula $[M_2N(L-L)S_2Cl_5]$ as suggested by analytical and IR data. These when solubilized in $POCl_3$ yielded the moisture sensitive adduct $[M(NSCl)Cl_3X'(L-L)].POCl_3$ similar to the behavior of $[M(NSCl)Cl_4]_2$.

The compounds in general were preserved at low temperature ($0^{\circ}C$) as they undergo slow decomposition at room temperature yielding a marroon/pinkish grey compound. This was further corroborated by the results of thermolysis experiments (vide infra). The gaseous products obtained by pyrolyzing the compound was hydrolyzed by bubbling in water and the halogen and sulfur contents were estimated. The results corresponded to the loss of a molecule of SCl_2 per molecule of the compound as also suggested by the loss of weight of the compound after thermolysis. It appears that the complexes lose a molecule of SCl yielding nitrido complexes from which another chloride ion could be lost to preserve the charge balance, similar to the earlier reported $M=N=S\diagdown Cl$ complexes.[2,3] These may further be reduced partially to other polymeric metal nitrides in +5 oxidation state.[6]

IV.2a   I.R. Spectra

The infra red spectra of all the compounds showed three medium to intense bands in the region 1000-900 cm^{-1} assignable to the stretching mode of M=N=S moiety (Fig. IV.1).[3,4,7,9] The bonding mode of NSCl moiety is further corroborated by the following chemical evidence.

The coordinatively unsaturated compound $[M(NSCl)Cl_4]_2$ had been shown to have $[M=N=S\backslash Cl]$ unit by X-ray crystal structure studies. The reaction of this compound with bipy or o-phen yielded compounds of the type $[M(NSCl)Cl_4(L-L)]$ which were found to be identical to the compounds synthesized by the procedure A(i). The identical nature of these compounds as shown by X-ray powder patterns, gives one sufficient reason to believe that the NSCl moiety in our compounds have a $[M=N=S\backslash Cl]$ type of bonding, assuming reactions of bipy or o-phen donot affect the bonding mode of (NSCl). Further the bands due to ν_{MNS} of $[M(NSCl)Cl_3X'-(L-L)]$ disappeared in the vibrational spectra of the products obtained after thermolysis and an intense band appeared at 940 cm^{-1} (M=Mo)/990 cm^{-1} (M=W) assignable to $\nu_{(M\equiv N)}$[6,10] (Fig. IV.2, IV.3). The shift of $\nu_{M\equiv N}$ band position to lower wave numbers compared to that of other nitrido compounds in +6 oxidation state (viz. > 1000 cm^{-1}) could be attributed to the partial reduction of M(VI) to M(V)[6] (vide infra). The assignments of bands due to lack of crystal structure are somewhat tentative and further studies are required to confirm their identity.

IV.2b Electronic Spectra

The electronic spectral features of the compounds are given in Table IV.1 (Fig. IV.4) and were typical of Mo(VI) and W(VI) complexes.[11] The spectra showed a band at around 250 nm assigned

to $\pi(X) \longrightarrow d\pi$ (M(VI)) charge transfer transition. The band at around 500 nm was found to be split in general and one of its components along with 380 nm band could be attributed to π(diimine) $\longrightarrow d\pi$(M(VI)) charge transfer transition. Its other component may possibly arise due to intraligand transition involving N=S$\diagdown$Cl moiety or due to charge transfer transition of the M=N=S$\diagdown$Cl$\diagdown$Cl unit.

IV.2c Magnetic Properties

All the compounds were found to be diamagnetic and their ESR spectra were recorded wherein no signal was obtained. This indicates the presence of metal in +6 oxidation state, substantiating further the linkage of NSCl as M=N=S$\diagdown$Cl . The products obtained after thermal decomposition exhibit partial paramagnetism and their magnetic moments fall in the range of 1.1-1.2 B.M. for Mo complexes and .8-.9 for the tungsten ones. The latter range is lower than the one expected for d^1 complexes suggesting partial reduction of M(VI) during decomposition of thionitrene complexes. The presence of M(V) in the decomposition products was further confirmed by the powder ESR spectra of the decomposed products which showed rhombic distortion.

In the compounds prepared in tetrahydrofuran, the solvated formulation viz. [M(NSCl)Cl$_3$X'(L-L). THF could be preferred over the coordinated one based on the following observations:

(i)   The NMR spectra showed practically no shift in the
        resonances of the THF protons as compared to that of
        the free THF molecule.

(ii)   The color and the m.p.'s of the compounds were almost
        similar to those of the compounds prepared in dichloro-
        methane.

The compounds were analyzed to $[M(NSCl)Cl_3X'(L-L)]$. THF
and the efforts to remove the solvated THF completely by different
means were unsuccessful.

On the basis of the foregoing discussions the compounds
were assigned the heptacoordinate structure $[M(NSCl)Cl_3X'(L-L)]$
with the metal ion in +6 oxidation state. Although seven coordi-
nation is commonly not encountered in the compounds of molybednum
and tungsten in higher oxidation states, it is however not
unlikely.[12]

It is interesting to observe the stability order of thio-
nitrene complexes of molybdenum and tungsten as $[MCl_4(NSCl)]_2 \ll$
$[MCl_3(NSCl)bipy] \simeq [MCl_3(NSCl)o-phen] < [MCl_4(NSCl)bipy] \simeq [MCl_4-$
$(NSCl)o-phen]$ $[M = Mo, W]$. The order could possibly be explained
on the presumption that the tendency of accumulation of the negat-
ive charge on the metal center lowers the stability of the complex.
Cl^- ions push the electrons to the metal center both as a σ- and
π donor ligand while the ligands like bipyridine and o-phenanthro-
line are good σ-donor but they are good π-acids and remove the

charge back from the metal center in their π^* orbitals. There will, therefore, be more depletion of negative charge from the metal center of the bipy or phen complexes relative to that in pure chloro complexes. On similar grounds, the complexes having metal ions in the lower oxidation state (+5) should relatively be less stable compared to those having metal ions in +6 state because of the presence of one extra electron on the metal ion in +5 oxidation state. These complexes prefer to form nitrido complexes as their decomposition products in which three negative charges can be comfortably accomodated on the nitrogen atom by sharing and thereby shifting the charge from the metal and forming stable nitrid system. This process takes place by the ejection of one mole of SCl_2 from one mole of complex.

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Table IV.1. Color, Microanalysis, Thermolysis, and UV-Visible Data of Complexes

Sl. No.		Color	Elemental analysis in Exptl(Calcd)					Thermolysis loss Exptl (Calcd)			UV-visible data λ_{max}/nm
			C	H	N	S	X	loss in wt.	S	Cl	
1.	[Mo(NSCl)Cl$_4$(Bipy)]	G	25.1 (25.3)	1.7 (1.6)	8.7 (8.8)	6.4 (6.7)	37.4 (37.1)	22.8 (21.6)	6.3 (6.7)	14.6 (14.9)	250,320,380, 476,510
2.	[Mo(NSCl)Cl$_3$Br(Bipy)]	GB	23.1 (23.0)	1.7 (1.5)	8.4 (8.0)	5.7 (6.1)	41.7 (42.6)	20.9 (19.7)	5.2 (6.1)	13.8 (13.6)	240,318,390, 476,515
3.	[Mo(NSCl)Cl$_4$(o-phen)]	G	29.4 (28.8)	2.1 (1.6)	7.9 (8.4)	5.8 (6.4)	36.2 (35.4)	22.1 (20.6)	5.8 (6.4)	14.8 (14.2)	240,300,370, 475,510
4.	[Mo(NSCl)Cl$_3$Br(o-phen)]	GB	26.8 (26.4)	2.1 (1.4)	8.2 (7.9)	6.2 (5.9)	39.7 (40.8)	20.2 (18.9)	5.2 (5.9)	13.6 (13.0)	250,300,385, 475,520
5.	[W(NSCl)Cl$_4$bipy]	GR	21.6 (21.2)	1.8 (1.4)	7.2 (7.4)	5.9 (5.7)	30.9 (31.4)	19.4 (18.2)	5.2 (5.7)	13.2 (12.6)	250,310,380, 475,510
6.	[W(NSCl)Cl$_3$Brbipy]	O	19.2 (19.7)	1.9 (1.3)	6.4 (6.9)	5.6 (5.2)	36.1 (36.4)	18.2 (16.9)	5.0 (5.2)	13.0 (11.6)	255,320,375, 480,515
7.	[W(NSCl)Cl$_4$o-phen]	YB	24.7 (24.5)	1.4 (1.3)	6.8 (7.1)	5.1 (5.4)	29.8 (30.1)	18.9 (17.5)	5.0 (5.4)	12.5 (12.0)	250,315,380, 475,510
8.	[W(NSCl)Cl$_3$Bro-phen]	B	22.4 (22.7)	1.7 (1.2)	6.3 (6.6)	4.9 (5.0)	34.8 (35.0)	17.8 (16.3)	4.2 (5.0)	12.0 (11.2)	248,320,375, 475,520

G=green, GB=greenish brown, GR=greenish red, O=orange, YB=yellow brown, B=brown.

Table IV.2. I.R. Spectral bands of Representative Complexes

$[Mo(NSCl)Cl_3X'(L-L)]$		$[W(NSCl)Cl_3X'(L-L)]$		$[MoNCl_2X'(L-L)]$		$[WNCl_2X'(L-L)]$	
960(m)		970(m)		940(vs)		999(vs)	
940(m)	$\nu_{as}(MNS)$	940(m)	$\nu_{as}(WNS)$	900(m)	$\nu(Mo\equiv N)$	900(m)	$\nu(W\equiv N)$
915(m)		910(m)					
495(w)	ν_{SCl}	500(w)	ν_{SCl}				
440(w)	$\nu_s(MoNS)$	430(w)	$\nu_s(WNS)$				
350(s)		340(s)		350(m)		370(m)	
320(m)	ν_{Mo-Cl}	320(m)	ν_{W-Cl}	320(m)	ν_{Mo-Cl}	340(m)	ν_{W-Cl}
270(w)	δ_{NSCl}	270(w)	δ_{NSCl}				

IR bands due to coordinated 2,2'-bipyridine and 1,10-phenanthroline were observed in the expected region.

129
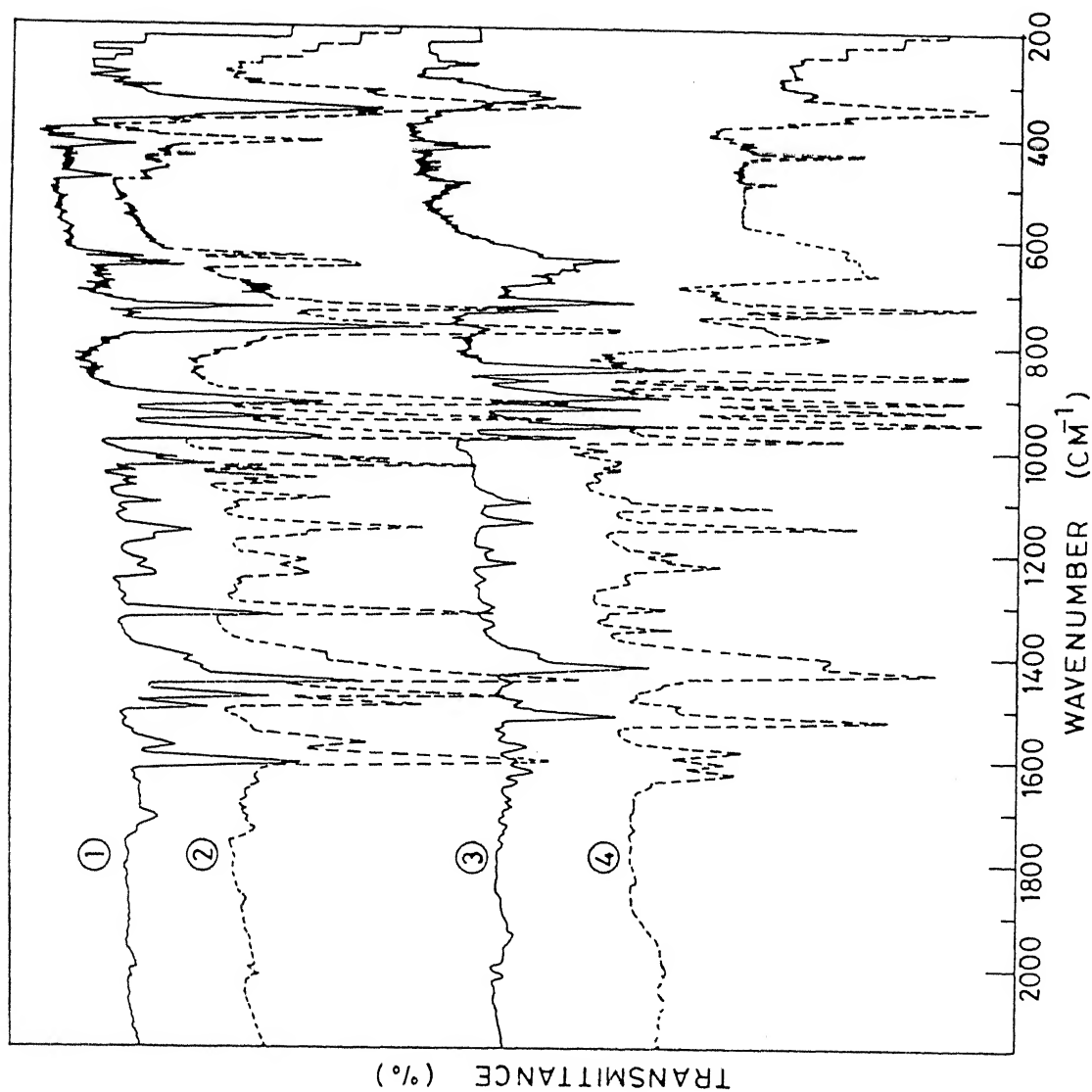
Fig.IV.1 Infrared spectra of [Mo(NSĆl)Cl₄bipy] from [Mo(CO)₃Cl₂(bipy)] (1), from [Mo(NSCl)Cl₄]₂ (2), Infrared spectra of [Mo(NSCl)Cl₄o-phen] from [Mo(CO)₃Cl₂(o-phen)] (3), from [Mo(NSCl)Cl₄]₂(4).
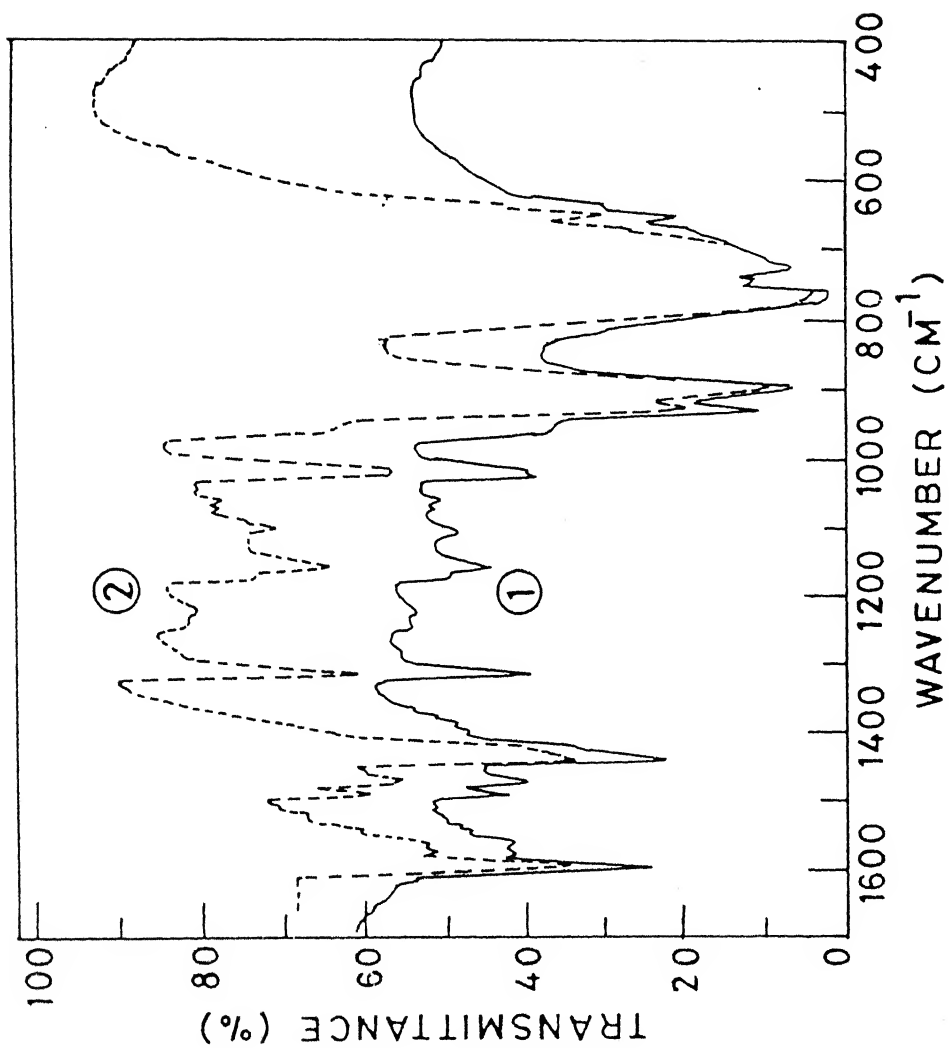
Fig.IV.2 Thermolysis product of [Mo(NSCl)Cl$_4$bipy] prepared from [Mo(CO)$_3$Cl$_2$bipy] (1), prepared from [Mo(NSCl)Cl$_4$]$_2$ (2).
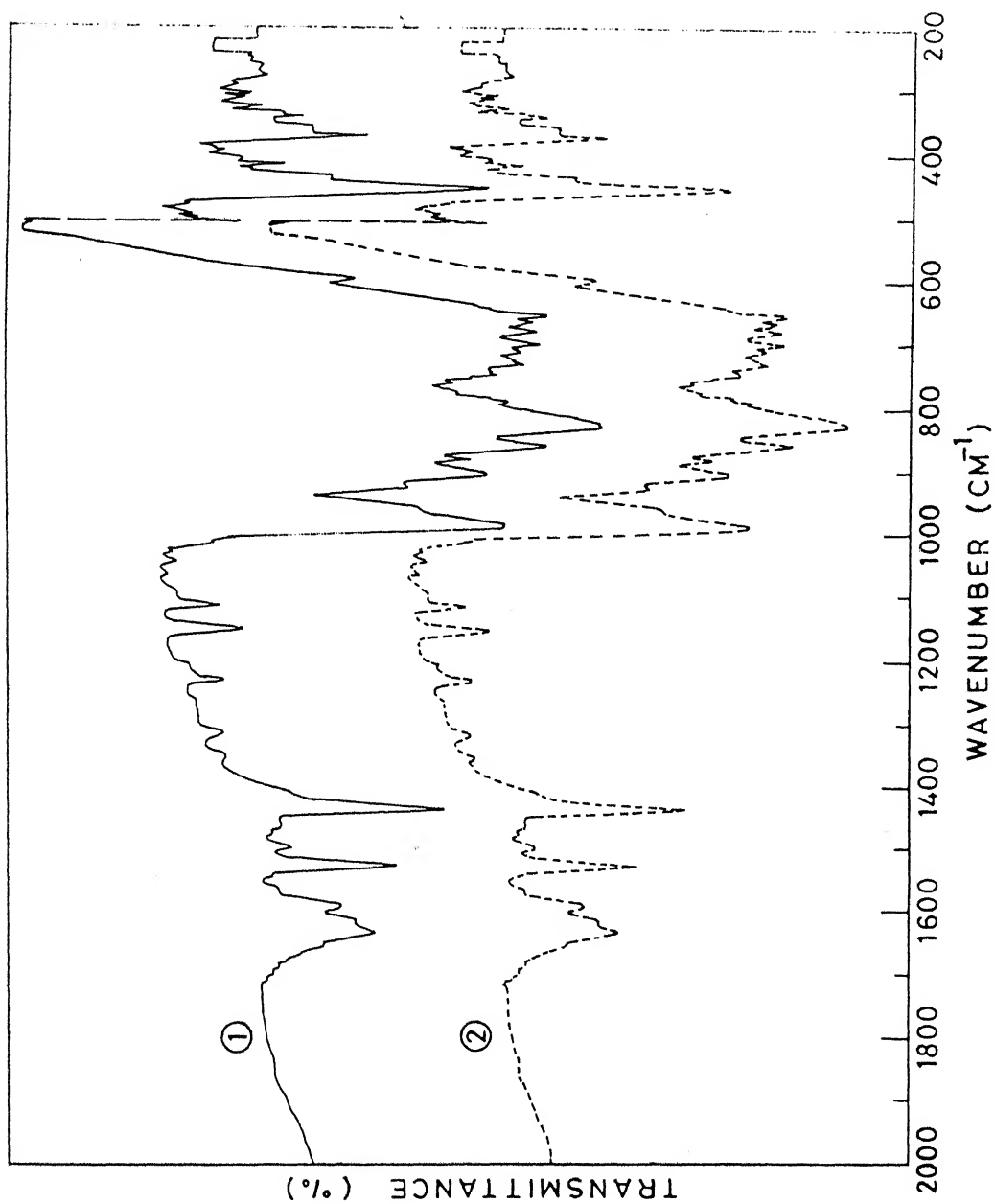
Fig.Iv.3 Thermolysis product of [W(NSCl)Cl$_4$bipy] prepared from [W(CO)$_3$Cl$_2$bipy] (1),

prepared from [W(NSCl)Cl$_4$]$_2$ (2).
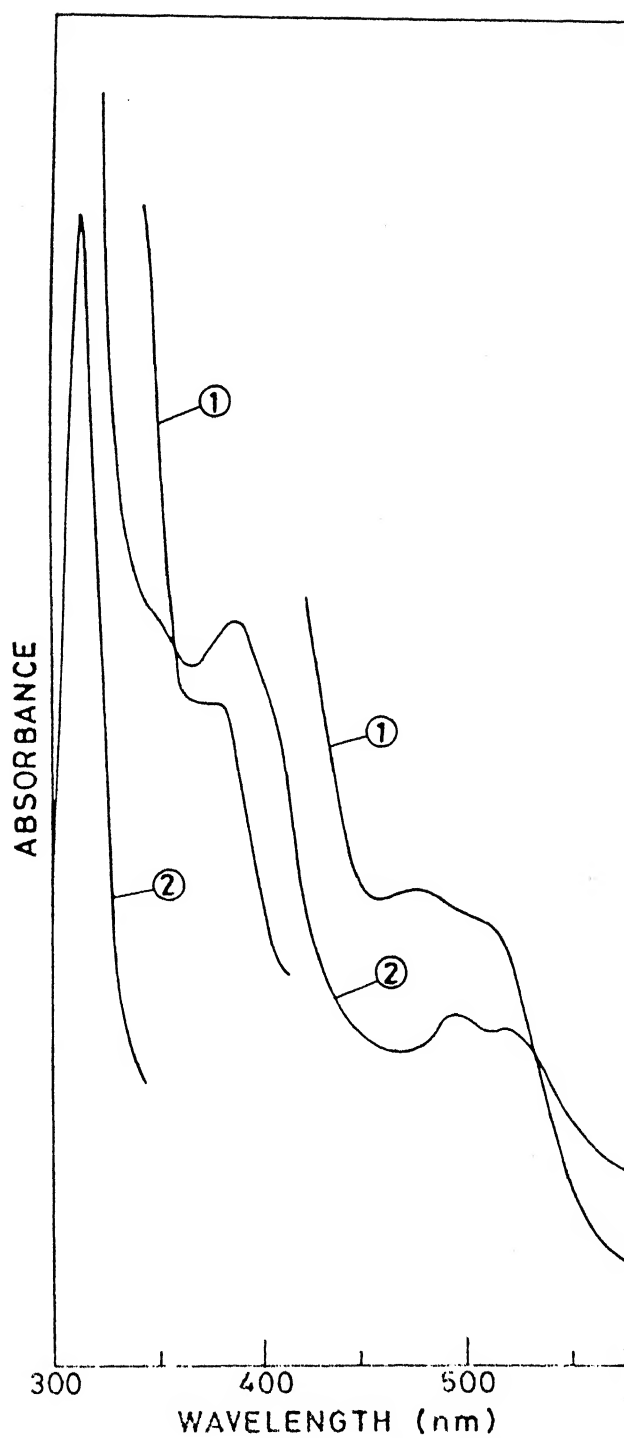
Fig.IV.4 Electronic spectra of [Mo(NSCl)Cl$_4$bipy] (1),

[W(NSCl)Cl$_4$bipy] (2).

Chapter - V

Synthetic and Bonding Aspects in Cyclothiazeno Molybdenum(V) Complexes

The chemistry of sulfur-nitrogen compounds has attracted attentions of both the theoreticians and the experimental chemists during the past decade. Though many workers have reported synthetic, IR and crystallographic studies of a number of metal complexes containing electron rich, relatively unstable sulfur-nitrogen rings and cages (S_2N_2, $N_3S_2{}^{3-}$, N_2S_3 etc) as coligands, no report aimed at understanding the nature of bonding in these complexes has appeared in the literature. The latter study warrants attention, in particular, for a possible solution of the problem, as to why metal complexation stabilizes these species. It is surprising that their electronic spectra and magnetic properties have also not been studied. The reason for the lack of such a study could be due to the fact that a large number of reported complexes are

diamagnetic which cannot be explored using techniques such as ESR. In this work, an attempt has therefore been made to synthesize and characterize paramagnetic molybdenum (V) complexes (d^1 system) whose ESR spectra will be particularly amenable to analysis. This chapter describes new molybdenum(V) pyridine and diimine derivatives of $[Mo(N_3S_2)Cl_3]_2$ and $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$ and is concerned with the discussion of the spectral (electronic and IR), magnetic data in terms of their coordination geometry and the bonding therein. Shifts from the free electron g value provided information about the spin-orbit mixing of the antibonding states with the ground state. The anisotropy of the metal nuclear hyperfine interactions has been related to the molecular orbital coefficients of the molecules. Results have indicated the importance of σ - and π-contributions in molybdenum-nitrogen bonds which involve 4d, $N_3S_2{}^{3-}$ and diimine or pyridine orbitals. A reduced coefficient for the metal requires the presence of ligand character in the wavefunctions describing the magnetic electron. This implies that the electron spends some time in the region of ligand nuclei and is subjected to spin-orbit effects.

A tentative explanation for the reduction of Mo from +6 to +5 oxidation state during the reactions has been suggested.

V.1 Experimental Section

(i) Materials

All the chemicals used were of AnalaR grade, Sephadex LH-20 (Sigma Chemical Co.), $Mo(CO)_6$, $MoCl_5$, pyridine, 2,2'-bipyridine and 1,10-phenanthroline were procured from Aldrich Chemical Co. $[Mo(N_3S_2)Cl_3]_2$ and $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$ were prepared by the published methods.[6,7] Reactions have been carried out under pure and dry dinitrogen using degassed solvents which were dried by standard methods.

(ii) Instrumentation

The microanalyses of the complexes were carried out at the Microanalytical Laboratory, I.I.T. Kanpur, India. The spectral details of IR(KBr) and UV-VIS(CH_2Cl_2, KBr) are given in chapter II. The magnetic susceptibility measurements were carried out on a Guoy balance using $Hg[Co(NCS)_4]$ as calibrant.

ESR spectra of diimine complexes were obtained in dichloromethane at room temperature and at 77K. For the pyridine complex, ESR spectra of polycrystalline sample were recorded at room temperature as well as low temperature. The low temperature spectra (polycrystalline sample at liquid nitrogen temperature) exhibited well resolved anisotropy. ESR measurements have been made on a Varian E-109 X-band spectrometer equipped with low temperature accessories. Other details about the instrument have been given elsewhere.[1] The

g values were calibrated against DPPH employing a dual ESR cavity.

The analysis of the molecular zeeman tensors (g and A, respectively) was done by fitting computer simulated line shapes to the experimental spectra. The line shape simulation was carried out on Dec-1090 computer using a program developed by Raghunathan and Sur[2] based on Iwaski's algorithm,[3] assuming the spin Hamiltonian of the form.

$$\mathcal{H}_s = \beta e.g.H.S + I.A.S - g_n\beta_n \ I.H. + I.Q.I \qquad (1)$$

where all the symbols have their usual meaning. The resonance field positions calculated by equation 1 are convoluted with a Gaussian line shape function with a peak to peak derivative line width appropriate to the spectrum being simulated. The simulated spectra were the sums of randomly oriented complexes with $I=0$ and $I=5/2$ isotopes weighted according to their natural abundances (75% and 25% respectively). The spectra are given in Fig. V.3–V.7. The results are given in Tables V.1 to V.3.

V.1a   Syntheses of Complexes

(i)   Synthesis of $[Mo(N_3S_2)Cl_2bipy]$

(a)   From $[Mo(N_3S_2)Cl_3]_2$

A suspension of freshly prepared $[Mo(N_3S_2)Cl_3]_2$ (ca 0.17 mmol) in 25 ml of dichloromethane was dissolved by stirring with

stoichiometric amount of 2,2'-bipyridine at 40°C for 2 h. The color of the solution turned to dark green. It was filtered to remove any insoluble impurities and the filtrate was concentrated under reduced pressure to about 5 ml. Excess petroleum ether (40°-60°) was added to the concentrate whereby a dark green compound was separated. It was filtered and the complex was then recrystallized using dichloromethane/petroleum ether. Its further purification was effected using Sephadex LH-20 column. The complex was dissolved in 5 ml of dichloromethane and the solution was sorbed onto a column (25 cm x 2.5 cm) prepared in dichloromethane: chloroform mixture (1:1, v/v). The green band formed at the top was eluted with dichloromethane. The eluent was concentrated to nearly 5 ml and the complex was precipitated by adding petroleum ether to the concentrate. It was separated by centrifugation, washed with petroleum ether and dried _in vacuo_. Some of the impurities remained sorbed on the top of the column and could not be eluted by any solvent. Yield of $[Mo(N_3S_2)Cl_2bipy]$, _ca_ 20%. Anal. Calcd for $[Mo(N_3S_2)Cl_2bipy]$: C, 27.9; H, 1.8; N, 16.3; S, 14.9; Cl, 16.5. Found: C, 28.2; H, 2.1; N, 16.5; S, 14.6; Cl, 16.7.

(b)   From $[Mo(N_3S_2)Cl_3]_2$-μ-S_2N_2

Freshly prepared $[Mo(N_3S_2)Cl_3]_2$-μ-S_2N_2 (0.17 mmol) and stoichiometric amount of 2,2'-bipyridine in dichloromethane (25 ml) were refluxed with stirring for 2 h whereby the complex $[Mo(N_3S_2)$-$Cl_3]_2$-μ-S_2N_2 went into solution (dark green). The remaining working procedure was the same as that given in [i(a)]. Yield _ca_ 80%.

(ii) Synthesis of $[Mo(N_3S_2)Cl_2$ o-phen$]$

(a)   From $[Mo(N_3S_2)Cl_3]_2$

The reaction was carried out by the same procedure as reported in $[i(a)]$ except that o-phenanthroline was used in place of 2,2'-bipyridine (yield of $[Mo(N_3S_2)Cl_2$o-phen$]$ ca 20% . Anal. Calcd. for $[Mo(N_3S_2)Cl_2$o-phen$]$: C, 31.7; H, 1.7; N, 15.4; S, 14.5; Cl, 15.6. Found: C, 31.2; H, 2,1; N, 15.5; S, 14.6; Cl, 15.1.

(b)   From $[Mo(N_3S_2)Cl_3]_2$-μ-S_2N_2

The reaction was carried out by the procedure as given in $[i(b)]$ except that o-phenanthroline was used in place of 2,2'-bipyridine. Yield, ca 80% .

(iii) Synthesis of $[Mo(N_3S_3)Cl_2(Py)_2]$

(a)   From $[Mo(N_3S_2)Cl_3]_2$

To the suspension of $[Mo(N_3S_2)Cl_3]_2$ (0.17 mmol) in dichloromethane (15 ml) excess of pyridine (2 ml) was added. The mixture was refluxed for 8-10 h whereby the color of the solution turned to dark green. The solution was filtered to remove any impurity. On keeping the filtrate, microcrystals were slowly formed which were separated by centrifugation, washed repeatedly with dichloromethane and dried in vacuo. Yield of $[Mo(N_3S_2)Cl_2(Py)_2]$, ca 15-20%.

Anal. Calcd for $[Mo(N_3S_2)Cl_2(Py)_2]$: C, 27.8; H, 2.3; N, 16.2; S, 14.8; Cl, 16.4. Found: C, 27.5; H, 2.5; N, 16.0; S, 14.3; Cl, 16.7.

(b) From $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$

To the suspension of $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$ in 15 ml dichloromethane (0.17 mmol) excess of pyridine (2 ml) was added and the mixture was refluxed for 8-10 h. The rest of the procedure was similar to that given in [iii(a)].

V.2 Results and Discussion

V.2a Reactivity of Complexes

Reactions of pyridine and diimines with $[Mo(N_3S_2)Cl_3]_2$ and $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$ proceed to form $[Mo(N_3S_2)Cl_2(Py)_2/bipy/o-phen]$ with simultaneous reduction of molybdenum from +6 to +5 oxidation state. Yields of the products using $[Mo(N_3S_2)Cl_3]_2$ as precursor were lower (ca 20%) than those obtained from $[Mo(N_3S_2)-Cl_3]_2-\mu-S_2N_2$ (ca 80%). In former reactions, the remaining compound seem to be a mixture of decomposed products. Effectively, no major change in the yields was observed by changing the reaction conditions. The reactions proceed as:

$$[\text{Mo}(N_3S_2)Cl_3]_2 + L/(L-L) \longrightarrow 2[\text{Mo}(N_3S_2)Cl_2(L)_2/(L-L)] +$$

$$\text{other products} \qquad (2)$$

$$[\text{Mo}(N_3S_2)Cl_3]_2^- \,^-S_2N_2 + L/(L-L) \longrightarrow 2[\text{Mo}(N_3S_2)Cl_2(L)_2/(L-L)] +$$

$$\text{other products} \qquad (3)$$
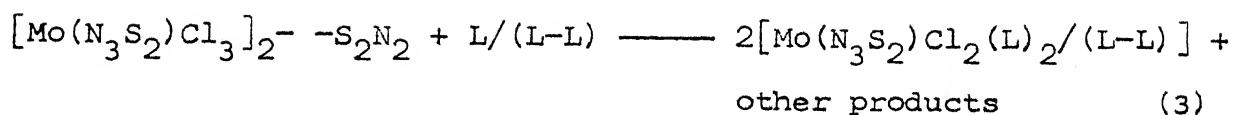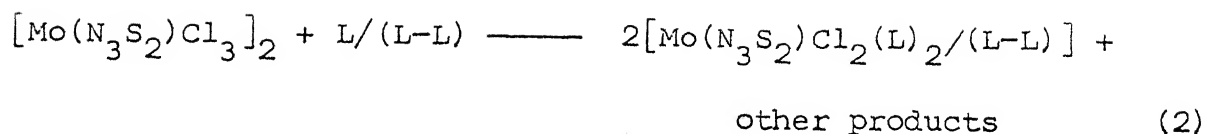
L = Py; L-L = bipy or o-phen.

Interesting feature of these reactions are the reduction of Mo(VI) to Mo(V) and the variation in the yields of the products. Though such reductions by amines and diimines are available in literature[4,5] the factors responsible for the enhanced yield in the reactions of $[\text{Mo}(N_3S_2)Cl_3]_2 {-}\mu{-}S_2N_2$ are somewhat obscure. Furthermore, the reaction of $[\text{Mo}(N_3S_2)Cl_3]_2$ with calculated amount of pyridine yields $[\text{Mo}(N_3S_2)Cl_3(\text{Py})]$.[6] While under our reaction conditions irrespective of the amount of diimine/pyridine, $[\text{Mo}(N_3S_2)Cl_3]_2 {-}\mu{-}S_2N_2$ yields the product with molybdenum in +5 oxidation state. The role played by S_2N_2 moiety (the only difference between the two reactants) in reducing Mo(VI) to Mo(V) and thereby enhancing the yields of the products can only be speculated. Though the reduction of Mo(VI) to Mo(V) in S_2N_2 bridged $[\text{Mo}(N_3S_2){-}Cl_3]_2 {-}\mu{-}S_2N_2$ has earlier been reported,[7] its mechanistic details are yet to be worked out. It is well known that linear, ring and cage type sulfur-nitrogen compounds are electron rich[8-12] and are highly susceptible to oxidation because of HOMO being π^*orbitals.[8-12] It is therefore, expected that S_2N_2 with similar properties may

possibly be a source of electrons for the reduction of molybdenum resulting in its oxidation to species which remain uncoordinated to the metal center. It may be thought that reactions of $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$ involve two steps (i) Substitution of S_2N_2 by pyridine or diimine with simultaneous oxidation of the liberated highly unstable S_2N_2 moiety and (ii) Consequent reduction of the metal center by the available electrons from the oxidation of S_2N_2. Thus the enhanced yield of the product in the latter reactions may possibly arise because of the presence of another source of electrons for the reduction process. The reduction by S_2N_2 is further supported by the results of the reactions of $[Mo(N_3S_2)Cl_3]_2$ and $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$ with PPh_4Cl. The former reaction yields the Mo(VI) compounds[13,14] while the latter Mo(V).[7]

The diimine complexes were soluble in common non-hydrocarbon solvents like $CHCl_3$, CH_2Cl_2 etc. They have a limited stability and slowly develop a yellowish tinge on keeping them for a few days in the open atmosphere. They are however more stable relative to $[Mo(N_3S_2)Cl_3]_2$ and $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$. The pyridine complex, insoluble in all common organic solvents was relatively more sensitive and became a blackish sticky mass. All the complexes can, however be preserved for a much longer time at low temperature. No effect was made to identify the final changed/decomposed products.

V.2b I.R. Spectra

Infra red spectra of all the complexes displayed bands of coordinated pyridine and diimines.[15] Besides these, they exhibited the characteristic pattern of bands due to vibrational modes of '$N_3S_2^{3-}$' group at around 960, 940, 910 cm^{-1} (Fig. V.1). No appreciable change in the $N_3S_2^{3-}$ group band positions was observed from those displayed by the spectra of $[Mo(N_3S_2)Cl_3]_2/[Mo(N_3S_2Cl_3]_2$·$\mu$-$S_2N_2$. Practically little shifts in the positions of $N_3S_2^{3-}$ bands[6,16] have been taken as one of the indications for the presence of $N_3S_2^{3-}$ moiety in our complexes having the same bond orders as those of the parent ones. The structure of the latter have already been determined by X-ray single crystal studies which indicated a N-bonded chelated '$N_3S_2^{3-}$' group with a large degree of double bond character in Mo-N bands.[6,7,16] The characteristic S_2N_2 bands (860 and 470 cm^{-1})[5] whose positions usually remain unshifted in the spectra of all the S_2N_2 complexes[17] disappeared from the spectra of the products. This suggested substitution of the bridging S_2N_2 group by diimine or pyridine molecules (The identity of the coordinated diimines was also confirmed by NMR). Furthermore, the terminal ν_{Mo-Cl} bands were identified by the presence of three bands (ν_{Mo-Cl}) of strong to medium intensity in the region 350-300 cm^{-1}.[6,16]

Although infrared spectroscopy has previously been used to distinguish between various isomers (cis and trans) of molybdenum complexes, the present study unfortunately did not enable us to

discriminate between the possible isomers of our complexes owing to the fact that their spectra exhibited ν_{Mo-Cl} bands in the same region where a few of the diimine or pyridine bands also appear. However, some information in this direction was obtained from the analysis of ESR data (<u>vide</u> <u>supra</u>).

V.2c   Electronic and ESR Spectra and Magnetic Properties

Electronic spectral data of pyridine (KBr pellet) and diimine (dichloromethane solution) complexes are given in Table V.2 (Fig. V.2). The band positions are not solvent dependent and the solutions of the complexes in CH_2Cl_2 obeyed Beer's law, thus ruling out the possibility of solvent complex interaction. The decomposition or the dissociation of the complexes in CH_2Cl_2 is ruled out by the fact that these complexes can be precipitated unchanged from their CH_2Cl_2 solutions.

These complexes gave an easily observed ESR spectra at room and at low temperature (77K) with practically no change in the line widths, etc. (Fig. V.3 to V.7). The absorption line (ESR) is anisotropic. In view of the fact that the molybdenum in the complexes has a d^1 configuration, in an approximately octahedral field, one would expect that the complexes will behave like other d^1 octahedral complexes with a degenerate $^2T_{2g}$ ground state whose ESR spectra are observed only at low temperatures.[18] On the grounds of observing the spectra at room temperature with practically no change in them at low temperatures, we have assumed that the ground

state in our complexes is an orbital singlet with a separation of a few thousand cm^{-1} below the first excited state.[19] Since the ESR spectra exhibited only two g values ($g_{||}$ and $g_\perp$) both at low and room temperatures, molybdenum in these complexes is presumably present in a rigid tetragonally distorted octahedral environment with two Cl$^-$ ions in trans and four nitrogen atoms (two of diimines, pyridines and two of $N_3S_2^{3-}$ ring) in equatorial positions (Fig. V.8(2)). The totally asymmetric structure with two chlorine atoms in cis positions is expected to show complete anisotropy and its ESR spectra would display three g values ($g_{xx} \neq g_{yy} \neq g_{zz}$).[20,21] Thus assuming trans structure, the complexes were taken to belong to D_{4h}/C_{4v} symmetry with the unpaired electron being present in dxy.[22,23] However, since the crystal field due to Cl$^-$ is expected to be smaller than that due to N, one may argue in favor of the electron being present in one of the degenerate (d_{xz}, d_{yz}) orbitals which have been split by the spin orbit coupling. But it should be noted that in case of degenerate (d_{xz}, d_{yz}) ground state, the g values should deviate considerably from 2.0023 and the complexes should have very little spin relaxation time resulting in very broad bands.[24] The fact that resonances are fairly narrow at room temperature[25] and with practically no change at low temperature (Fig. V.3-V.7) implies that the ground state is non degenerate and is well separated in energy from other d orbitals. It seems that crystal field distortion imposed by lattice forces results in d_{xy} becoming the lowest energy orbital. Other possible reasons in favor of the d_{xy} ground state orbital could be as follows:

(a) $N_3S_3^-$ ion (a 10-electron system) is electron rich with four electrons present in the antibonding orbitals.[8-12,27] The (MoN_3S_2) moiety in the present systems would be analogous to the $N_3S_3^-$ ion where one of the S atoms has been replaced by a Mo, forming a planar hetero-ring system. The X-ray single crystal structures of the molecules $[Mo(N_3S_2)Cl_3]_2$, $[Mo(N_3S_2)Cl_3THF]$, $[Mo(N_3S_2)Cl_3]_2^-$ $\mu-S_2N_2$ and $[Mo(N_3S_2)Cl_3Py]$ reveal that $N_3S_2^{3-}$ along with Mo atom forms a nearly planar six membered ring in these complexes. The orders of both Mo—N bonds is approximately two (Fig. V.8(1)). The double bonds between Mo and N are formed by the overlap of d_{xz}, d_{yz} orbitals of Mo with the p_z orbitals of sulfur and nitrogen atoms of the ring forming π and π^* orbitals. Consequently, the latter antibonding orbital might have become raised above dxy resulting in the lone electron of Mo(V) in dxy.

(b) The ground state in $[MoCl_6]^-$ and $[MoCl_4(OR)_2]^-$ is assumed to be singlet with unpaired electron in dxy. This is presumed to arise through considerable distortion in the molecular frame work either through lattice forces or the jahn teller effect.[19,28-30] Even if there is axial distortion in the molecule, dxz, dyz should have been the ground state but its symmetry has been assumed to be C_{4v} because of the similarity of its ESR spectrum to those of molybdenyl complex $[MoOCl_5]^{2-}$.[19,28-30] Similar arguments may be put forward in our cases also because of the similarity of the ESR spectra of our complexes to those of other molybdenyl ones.

(c) The value of $A > B$ also tentatively rule out the degenerate dxz, dyz ground state.[31]

Thus in the following discussion and calculations, the molecular symmetry of the complexes in the solid state has been assumed to be C_{4v}/D_{4h} with dxy as their ground state.

(i) Electronic Spectra

If X and Y axes are defined along the equatorial Mo-N bonds, the Z-axis along the Mo-Cl bond and the ground state with predominently dxy in character, the lowest energy band in the spectra ($12,000$ cm^{-1}, $\varepsilon < 150$ cm^{-1}M^{-1}) was assigned to d_{xy} (b_2^*) $\longrightarrow$ d_{xz}, d_{yz} (e^*) transition (d_{xz}, d_{yz} have been assumed to be mixed orbitals having contributions from metal d orbitals and p_z orbitals of N and S atoms of the $N_3S_2^{3-}$ ring). The second weak band around $20,000$ cm^{-1} ($\varepsilon < 1000$ cm^{-1}M^{-1}) has been assigned to d_{xy} (b_2^*) $\longrightarrow$ $d_{x^2-y^2}$ (b_1^*).[19] The latter transition being forbidden, would be expected to be of low intensity. However, the intensity stealing from the neighboring charge transfer bands around $25,000$ cm^{-1} and/or symmetry lowering may be responsible for the increase in intensity of the latter band. Another, broad band is also present around $25,000$ cm^{-1}. The value of its extinction coefficient ($\varepsilon > 3000$ cm^{-1}M^{-1}) suggest that the band may be of the charge transfer type. Although we do not attempt to make a definite assignments for these bands, they are presumably associated with the

transition of the type halogen $(\pi) \longrightarrow d_{xz}$, d_{yz} (e^*) or d_{z^2} or d_{xy} (b_2^*) (LMCT band) in keeping with Jorgensen's assignments[32] of the electron transfer spectra of the transition metal hexa-halogen salts and/or with the intraligand transitions $(\pi \longrightarrow \pi^*$ of pyridine, diimines and/or $N_3S_2^{3-}$ group). A band at around 16,300 cm^{-1} ($\varepsilon \geqslant 2500$ cm^{-1}M^{-1}) could possibly be due to π(diimine) $\longrightarrow$ M(d) transition was found to be asymmetric in the solution spectra of the diimine Mo(V) complexes. A shoulder appeared towards the lower energy side might be assigned to $b_1 \longrightarrow b_2^*$ transition (bonding molecular orbital $\longrightarrow d_{xy}$).

Since the complexes have nd^1 configuration, two weak bands in the 12,000 cm^{-1} – 24,000 cm^{-1} region have been assigned to the components of transition $^2T_{2g} \longrightarrow {}^2E_g$ (O_h symmetry) in a ligand field of symmetry C_{4v}.[33] We have taken 10 Dq as the higher energy component of the split band, viz. $b_2^* \longrightarrow b_1^*$ (in C_{4v} symmetry).

(ii) Magnetic Properties

Magnetic moments of all the complexes are listed in Table V.1. For a ligand field of O_h symmetry, and using the free ion spin-orbit coupling constant (λ_o) as 1030 cm^{-1}, one would expect molybdenum (V) ion to have a room temperature magnetic moment of about 0.9 B.M. However, in a complex, the value of λ is usually much less than 1030 cm^{-1} which results in higher magnetic moments of the complexes. Furthermore, the electronic spectral and ESR

data support a reduction in the ligand field symmetry from O_h atleast to D_{4h} or C_{4v} which will further enhance the value of μ_{eff}. It is therefore expected to observe magnetic moments closer to the spin only value, which have experimentally been found.

Under the simultaneous perturbation by spin-orbit coupling and an axial component in the ligand field, it has been assumed that the $^2T_{2g}$ ground state term is split with the singlet dxy as the ground state (<u>vide infra</u>). Symmetry lowering will result in anisotropy of g tensor (cf. ESR data). Assuming C_{4v} symmetry of the ligand field and including TIP term, Ballhausen[34] calculated the magnetic susceptibility of d^1 system. Using the same expressions and with the values of $g_{||}$ and $g_{\perp}$ and energy distances between the various states, obtained from ESR and electronic spectral data, respectively, we have estimated the magnetic moment values of the complexes. The values are in good agreement within the experimental error, which further confirms symmetry lowering and +5 oxidation state of molybdenum in the complexes.

(iii)   <u>ESR Spectra</u>

The ESR spectra of diimine cyclothiazeno complexes in dichloromethane at room temperature were well resolved, consisting of a central intense line corresponding to the molybdenum (I=0) nucleus and six relatively weak hyperfine lines on either side of the central line arising from ^{95,97}Mo (I=5/2) (Fig. V.3, V.5).

The frozen solution spectra of the diimine complexes and the polycrystalline sample of diimine and pyridine complexes can be interpreted in terms of the axial spin Hamiltonian,

$$\mathcal{H}_s = g_{||} \cdot \beta \cdot H_z \cdot S_z + g_\perp \beta (H_x S_x + H_y S_y) + A \cdot I_z \cdot S_z +$$
$$B(I_x S_x + I_y S_y) \qquad (4)$$

In solution at room temperature, the anisotropies are averaged to zero, the spin Hamiltonian then becomes

$$\mathcal{H}_s = \langle g \rangle \cdot \beta H \cdot S + \langle A \rangle \cdot I \cdot S \qquad (5)$$

The spectra in Fig.V.4,V.6,V.7 are characteristic of axially symmetric g tensors with $g_\perp > g_{||}$. For frozen solution/polycrystalline spectra $\langle g \rangle = 1/3 \ (g_{||} + 2 g_\perp)$ and $\langle A \rangle = 1/3 (A + 2B)$. The close agreement between the frozen solution/polycrystalline sample and dichloromethane solution values of $\langle g \rangle$ and $\langle A \rangle$ for diimine complexes provide a strong evidence for the fact that the same species are present in both. Furthermore, agreement in the case of $\langle A \rangle$ indicates the same sign for both A and B.

All the cyclothiazeno molybdenum(V) compounds reported herein give an easily observable spectrum at room temperature. As discussed earlier, it is believed that the unpaired electron is in d_{xy} orbital which is well separated in energy from other d orbitals.

Assuming C_{4v} symmetry (<u>vide</u> <u>infra</u>), of the many molecular orbitals formed by the overlap of metal orbitals, p orbitals of nitrogen, chlorine and sulfur, those which are necessary for the discussion of the ESR spectra are the ones which transform themselves into b_1, b_2 and e representations. The LCAO-MO functions for the orbitals are:

$$\left| B_2^* \right\rangle = \beta_2 \left| d_{xy} \right\rangle - \beta_2' \left| \phi_{b_2} \right\rangle \tag{6}$$

$$\left| B_1^* \right\rangle = \beta_1 \left| d_{x^2-y^2} \right\rangle - \beta_1' \left| \phi_{b_1} \right\rangle \tag{7}$$

$$\left| E^* \right\rangle = \varepsilon \left| d_{xz}, d_{yz} \right\rangle - \left| \phi_{ex,ey} \right\rangle \tag{8}$$

where ϕ are the ligand group orbitals of appropriate symmetry. The starred orbitals are antibonding orbitals. These basis functions are perturbed by the spin-orbit coupling, Zeeman and hyperfine interactions. The ESR parameters may be expressed as functions of coefficients of these orbitals. We have used the expressions derived by D.eArmond et al.[35] (cf. Appendix A-III). We have also attempted to calculate the molecular orbital coefficients using expressions of Kon and Sharpless[36] (cf. Appendix A-IV) who have derived them by including the transition b_1 (bonding orbitals) $\longrightarrow$ b_2^* and ignoring overlap terms. The results, thus obtained are compared. In the expressions, the notations have their usual meanings. The value of the Fermi isotropic interaction, k(Kappa) was obtained from the equation.[37,38]

$$\langle A \rangle = -Pk - (2.0023 - \langle g \rangle)P \qquad (9)$$

The spin orbit coupling constant λ_M for [95,97]Mo was taken to be that of Mo^{3+} since the effective charge on molybdenum is expected to be less than its oxidation number by two units and has been shown to be 820 cm^{-1}.[35,39] (we have also compared the results of the calculations using lower values of λ_M (515 cm^{-1}) as obtained from magnetic moment data). The spin orbit coupling constant parameter λ_L for nitrogen is the one given by McClure.[40] The values of the electronic energy transitions for $b_2^* \longrightarrow b_1^*$, $b_2^* \longrightarrow e^*$ and $b_1 \longrightarrow b_2^*$ have been evaluated from the electronic spectra of the compounds (vide infra). The overlap integral values have been assumed the same for our system as used by Manoharan and Rogers.[39] Though our system is entirely different from the one described by them and one would not expect overlap integrals to be the same, it seems reasonable to accept them as such. Moreover, the values of the bonding coefficients were not significantly altered when the overlap integral values were changed one at a time to the extent of $\pm$ 0.04 (total change of 0.08). This indicates that the assumed overlap integral values are possibly correct. Since we have made several assumptions in the calculations, the bonding coefficients thus obtained will not be highly accurate but we believe that they will have the correct order of magnitude.

With the aid of the equations[35], the bonding coefficients were calculated for $[Mo(N_3S_2)Cl_2bipy]$, $[Mo(N_3S_2)Cl_2o\text{-}phen]$ and $[Mo(N_3S_2)Cl_2(Py)_2]$ by an iterative procedure using parameters given in Table V.2 (cf. Appendix A-III). A similar iterative procedure was used to calculate the bonding coefficients with the help of equations given by Kon and Sharpless[36] (cf. Appendix A-IV) using the same parameters (Table V.2). The results are given in Table V.3.
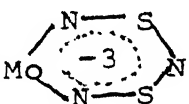
Though the values obtained by using different set of equations derived by different workers using various assumptions and different λ_M values were slightly different but the qualitative picture they provide about the nature of bonding in these complexes is the same. However, if one ignores the overlap integrals and does not consider $b_1 \longrightarrow b_2^*$ transition term in the equations of Kon and Sharpless, the values of β_1 and ε are lowered appreciably but the value of β_2 remained practically the same.

From the results compiled in Table V.3, one can draw following inferences.

(1) The value of β_2, the coefficients for the metal part of the in plane π bonding between metal $4 d_{xy}$ and ligand π orbitals lie between .93-.98. This indicates that the amount of in plane π bonding is very small. This is expected since in the trans structure (C_{4v} or D_{4h}) the nitrogen atoms of the ligands like bipyridine, o-phenanthroline or pyridine do not have orbitals

available for bonding but do have in the cis structure. This
further substantiate our assumption of axial distortion in the
complexes.

(2) The value of β_1, which indicates the extent of in plane
bonding between the metal $d_{x^2-y^2}$ orbitals and the ligand σ orbi-
tals appears to be relatively more sensitive to the changes.
However, the values obtained either from D.eArmond's equations or
from Kon and Sharpless's equations, reveal a high degree of co-
valency, in the Mo-N bonds. This can be accounted for by the fact
that $N_3S_2^{3-}$ is an electron rich system and should be highly polari-
zable. It is therefore expected that σ electrons present on
terminal nitrogen atoms should be highly polarized by Mo(V) which
has very high ionic potential owing to its +5 charge and small

radius. It is further substantiated by the fact that Mo

ring in the complex may be taken as a derivative of $N_3S_3^-$ ion in
which one of the S^+ ion is substituted by Mo^{+5} ion having relati-
vely higher polarizing power than S^+. $N_3S_3^-$ ion has S-N σ bond,
one therefore expects relatively more covalency in Mo-N bonds than
S-N bond. Furthermore, ligands like bipyridine, o-phenanthroline
and pyridine are highly basic in nature.

(3) The value of ξ is a measure of the extent of out of plane π-
bonding between the metal $4d_{xz}$ and $4d_{yz}$ orbitals and the ligand
π orbitals. The low value reveal the extensive out of plane

π-delocalization from the equatorial ligands to molybdenum d_{xz} and d_{yz} orbitals. This is apparently the result of the proximity of the empty d_{xz} and d_{yz} orbitals on the metal to the full p_z orbitals on the nitrogen atoms or to the fully occupied antibonding π^* orbitals of the $N_3S_2^{3-}$ ion. dxz and dyz will partake equally strongly with the formation of highly delocalized out of plane bonds like benzene or $N_3S_3^-$ ion. This fact is very well proved by the fact that in the molecules like $[Mo(N_3S_2)Cl_3]_2$, $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$ and $[Mo(N_3S_2)Cl_3(Py)]$, Mo-N bonds have very high double bond character.[6,7,16] It is because of this out of plane interaction between d_{xz}, d_{yz} orbitals of metal and the fully occupied ligand antibonding π^* orbitals which may be responsible to bring antibonding character in d_{xz}, d_{yz} orbitals and raise them above the metal d_{xy} orbitals as discussed earlier.

(4) In our system, it is found that $g_\perp > g_{||}$. It must be related to the nature of the bonding. This can be explained by assuming (a) relatively low lying excited electronic configuration in which the electron from the filled molecular orbital is excited to the half filled orbital, e.g. $b_1 \longrightarrow b_2^*$ or/and (b) the spin orbit interaction of the ligand λ_N (very low value of λ_N). Either one or both of the factors may be responsible for making $g_\perp > g_{||}$. We emphasize here that in making $g_\perp > g_{||}$, it is the entire term $(-\lambda_L \beta_2'\beta_1')$ which is important and not the individual values of each factor.

From the bonding coefficients explained above, it is not inappropriate to calculate spin densities on each N atom quantitatively. The unpaired electron population on all the four N orbitals has been calculated by the Mulliken Population analysis[41] (Table V.3). Their values are in the order Mo-o-phen $\rangle$ Mo-bipy $\rangle$ Mo-Py.

A limited amount of information on the electronic structure of the complexes has been obtained from the data we have got from IR, electronic spectral, magnetic susceptibility and ESR data. These reveal axial asymmetry in the complexes. Assuming C_{4v} symmetry, the ground state is $b_2(d_{xy})$. The lone electron is found only a little over the ligand molecules in the equatorial plane. d_{xz} and d_{yz} orbitals appear to be engaged in out of plane bonding with the ligand π^* orbitals. This corroborates the double bond character of the Mo-N bonds in $[Mo(N_3S_2)Cl_3]_2$ and $[Mo(N_3S_2)Cl_3]_2-\mu-S_2N_2$. We believe that in making out of plane bond, d_{xz}, d_{yz} orbitals are not only involved in interacting with the orbitals of $N_3S_2^{3-}$ ring but the electrons are also delocalized over π^* orbitals of the bipyridine, o-phenanthroline or pyridine moieties providing a completely delocalized π system over the atoms in equatorial plane. This will make all the four nitrogen atoms equivalent. $\Delta g_{||}$ and $\Delta g_{\perp}$ could be used to determine the extent of spin-orbit mixing of the antibonding states with the ground state. The anisotropy of the metal-nuclear hyperfine interaction has been shown to be

related to the molecular orbital coefficient of the ground state and to $\langle r^{-3} \rangle$ for unpaired electrons. The spin orbit effects arising from the presence of ligand character in the wave-functions describing the magnetic electrons implies that electron spends sometime in the region of ligand nuclei.

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Table V.1 Magnetic Susceptibility data

	$\mu_{exptl.}^{\neq}$ (B.M.)	$\mu_{calcd.}^{*}$ (B.M.)
$[Mo(N_3S_2)Cl_2bipy]$	1.71	1.74
$[Mo(N_3S_2)Cl_2ophen]$	1.73	1.76
$[Mo(N_3S_2)Cl_2(Py)_2]$	1.73	1.76

$\neq$ μ includes TIP and Diamagnetic correction.

$*$ μ calculated by the equations given in Ref. 34..

Table V.2 Parameters used in calculating bonding coefficients

Parameter	Mo(N$_3$S$_2$)Cl$_2$bipy]	Mo(N$_3$S$_2$)Cl$_2$ophen]	Mo(N$_3$S$_2$)Cl$_2$(p$_3$
$g_{\parallel}$	1.9498	1.9498	1.9493
$g_{\perp}$	1.9650	1.9647	1.9653
$\langle g \rangle$	1.9605	1.9617	1.9600
A(cm^{-1})	.007475	.007275	.007575
B(cm^{-1})	.002675	.003025	.002875
$\langle A \rangle$	.004400	.004575	.00444
λ_{Mo}(cm^{-1})	820	820	820
λ_{N}(cm^{-1})	70	70	70
$\Delta E(b_2^* \rightarrow b_1^*)$(cm^{-1})	21100	21825	21592
$\Delta E(b_2^* \rightarrow e^*)$(cm^{-1})	12300	12578	12603
$\Delta E(b_1 \rightarrow b_2^*)$(cm^{-1})	16100	16150	16300
Sb_2	.12	.12	.12
Sb_1	.16	.16	.16
Se	.20	.20	.20
K	.8	.82	.78
P	$-$.0055	$-$.0055	$-$.0055

Table V.3 Bonding coefficients   Using the Equations of DeArmond et al. , S ≠ 0

	$\lambda'_M = 820 \text{ cm}^{-1}$			$\lambda'_M = 515 \text{ cm}^{-1}$		
Parameter	Mo(N$_3$S$_2$)Cl$_2$bipy]	Mo(N$_3$S$_2$)Cl$_2$o-phen]	Mo(N$_3$S$_2$)Cl$_2$py$_2$]	Mo(N$_3$S$_2$)Cl$_2$bipy]	Mo(N$_3$S$_2$)Cl$_2$o-phen]	Mo(N$_3$S$_2$)Cl$_2$py$_2$]
β_1	.683	.720	.680	.763	.778	.734
β_2	.938	.924	.958	.948	.937	.969
ϵ	.686	.704	.665	.807	.837	.803
Spin density	4.24%	5.06%	3.28%	3.80%	4.24%	2.80%
Using the Equations of DeArmond et al., S = 0						
β_1	.502	.516	.471	.606	.627	.579
β_2	.961	.948	.982	.963	.950	.983
ϵ	.534	.556	.543	.693	.713	.684
Using Kon and Sharpless Equations, S = 0, $b_1 \rightarrow b_2^*$ transition included						
β_1	.891	.894	.862	.872	.884	.826
β_2	.923	.933	.943	.952	.968	.977
ϵ	.785	.796	.791	.767	.818	.812

s = Overlap integral.
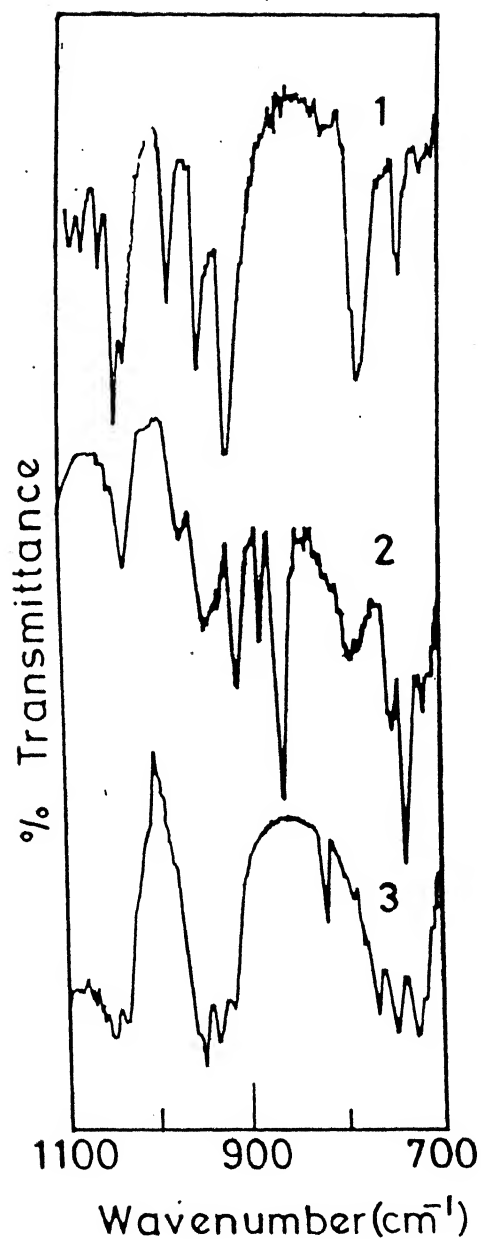
Fig.V.1   Infrared spectra of complexes in the region 1100-700 cm^{-1}.

(1) $[Mo(N_3S_2)Cl_2bipy]$, (2) $[Mo(N_3S_2)Cl_2 o\text{-phen}]$,

(3) $[Mo(N_3S_2)Cl_2(Py)_2]$
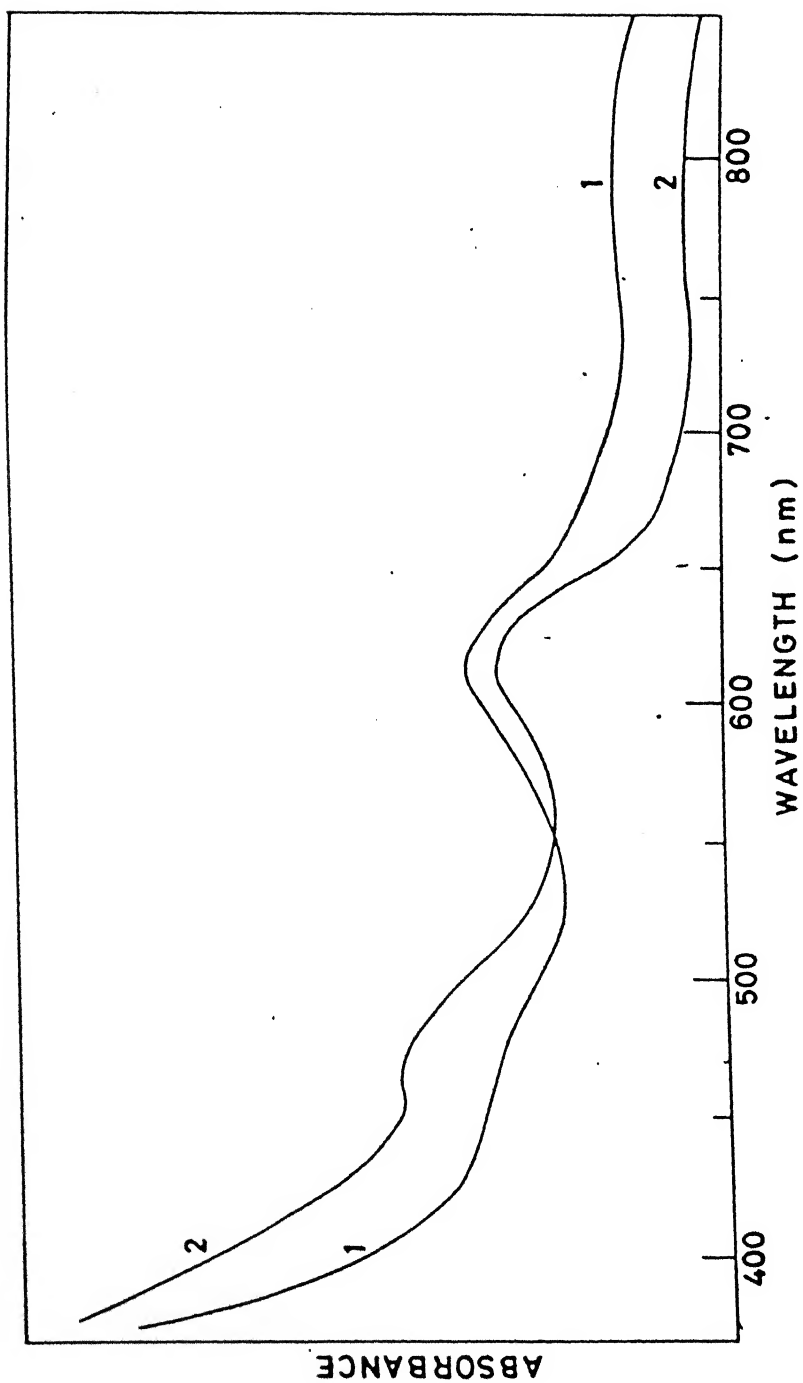
Fig. V.2 Electronic spectra of (1) $[Mo(N_3S_2)Cl_2bipy]$,

(2) $[Mo(N_3S_2)Cl_2o-phen]$
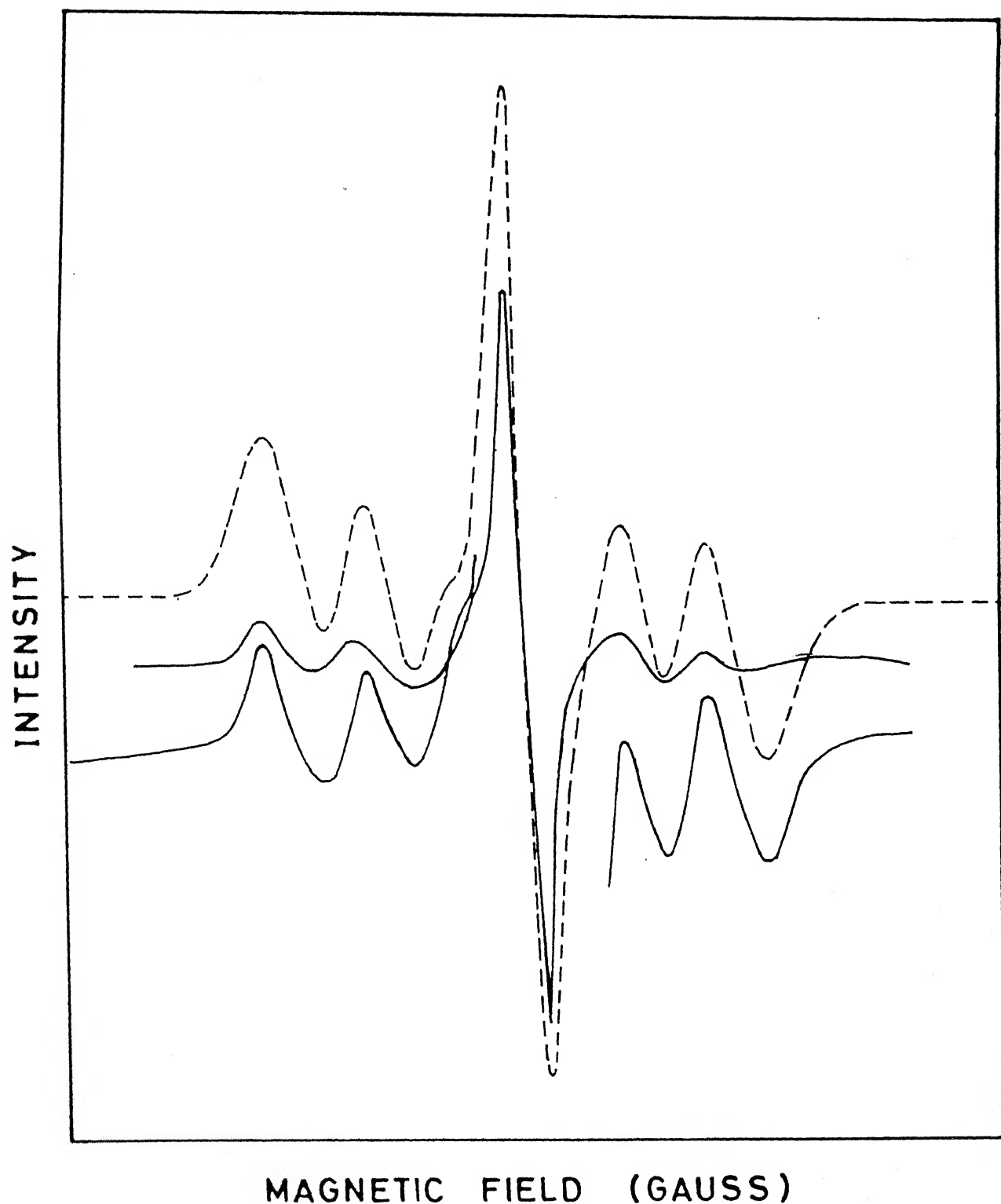
Fig.V.3 ESR spectra of $[Mo(N_3S_2)Cl_2bipy]$ in CH_2Cl_2 at 298 K.

(————) Experimental (————) Simulated.
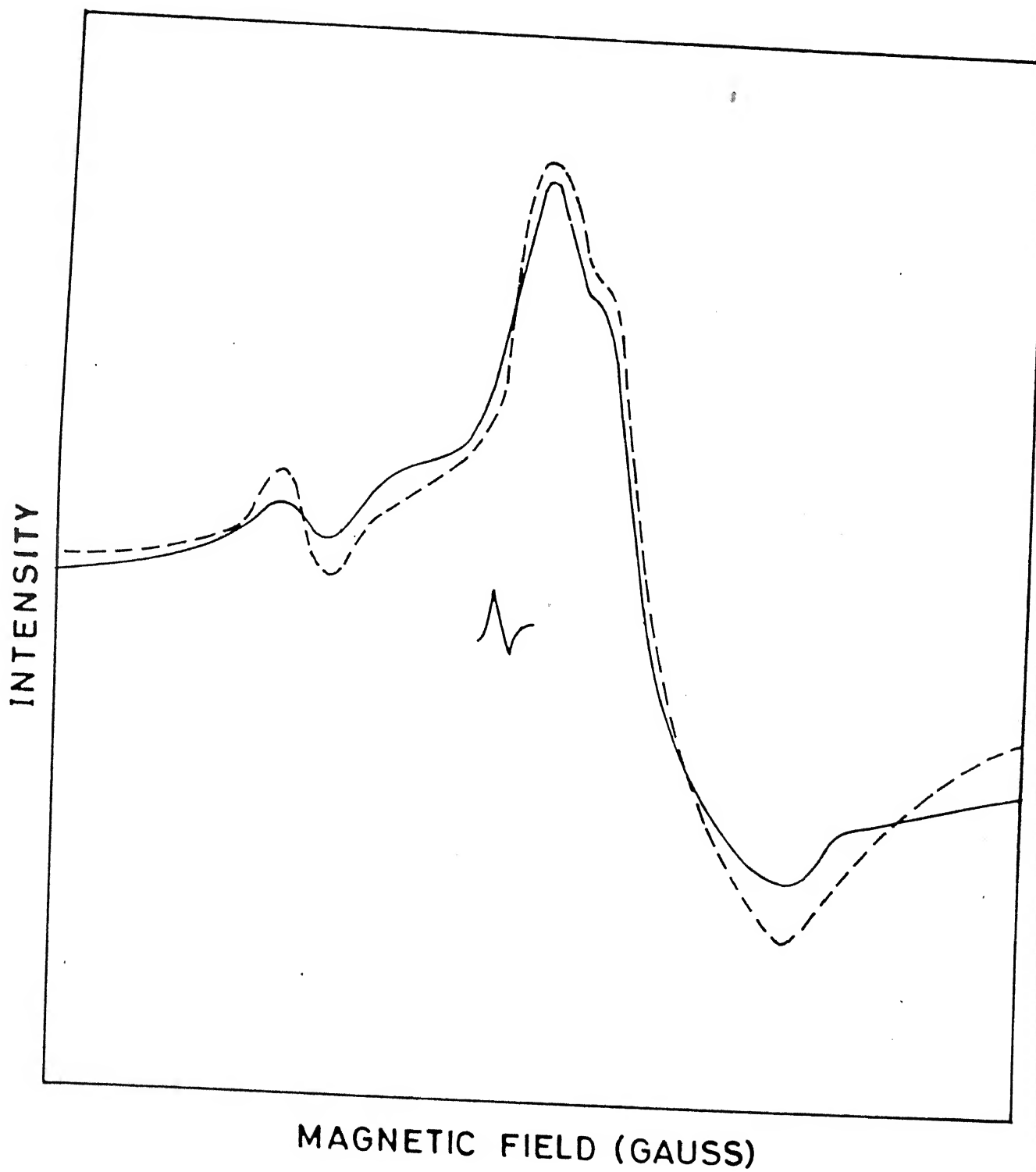
Fig.V.4 ESR spectra of $[Mo(N_3S_2)Cl_2bipy]$ in CH_2Cl_2 at 77 K.

(————) Experimental (————) Simulated.
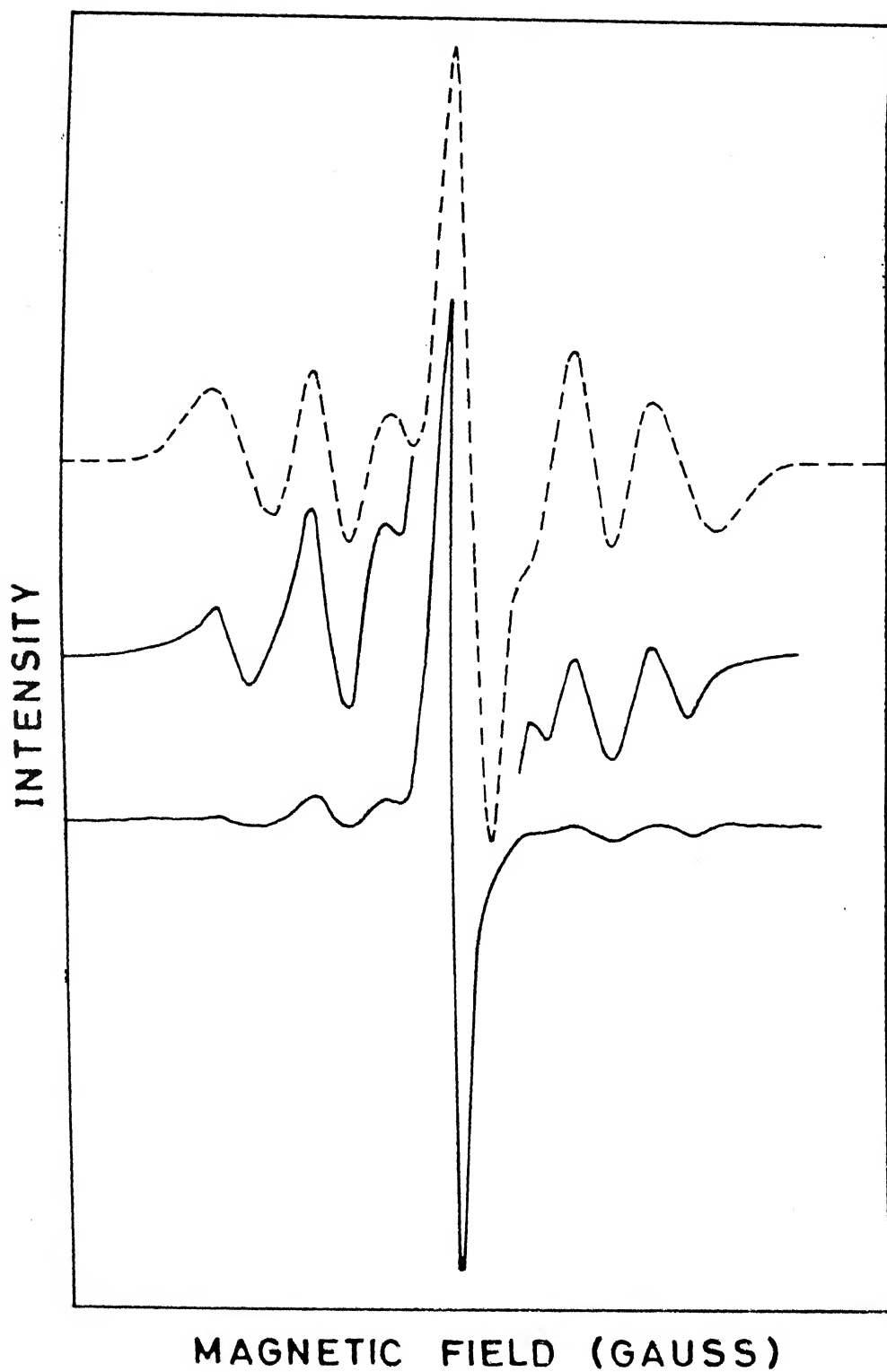
Fig.V.5 ESR spectra of $[Mo(N_3S_2)Cl_2o\text{-phen}]$ in CH_2Cl_2 at 298 K.

(————————) Experimental (————————) Simulated.
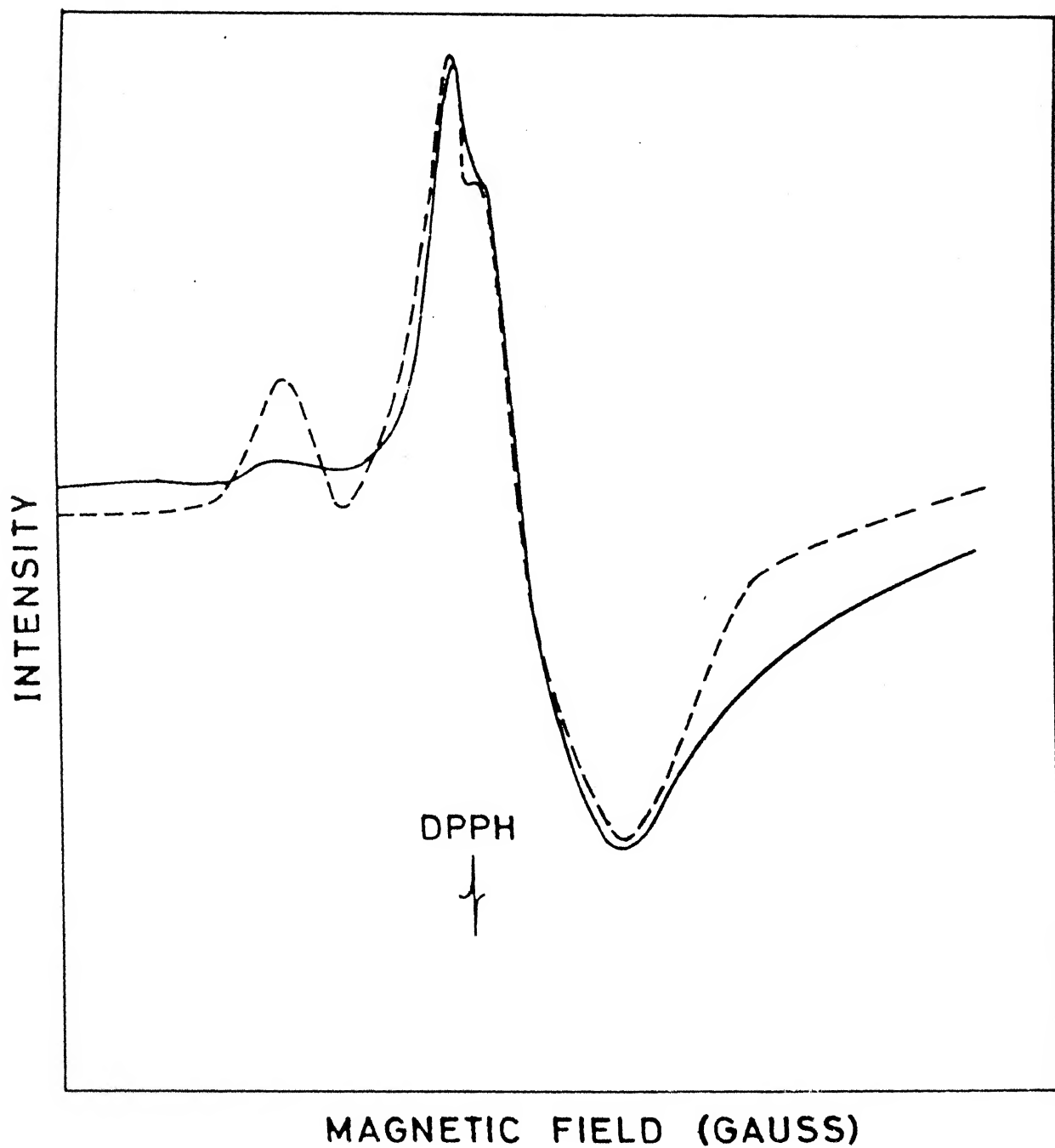
Fig.V.6   ESR spectra of $[Mo(N_3S_2)Cl_2 o\text{-phen}]$ in CH_2Cl_2 at 77 K.

(————) Experimental (— — —) Simulated.
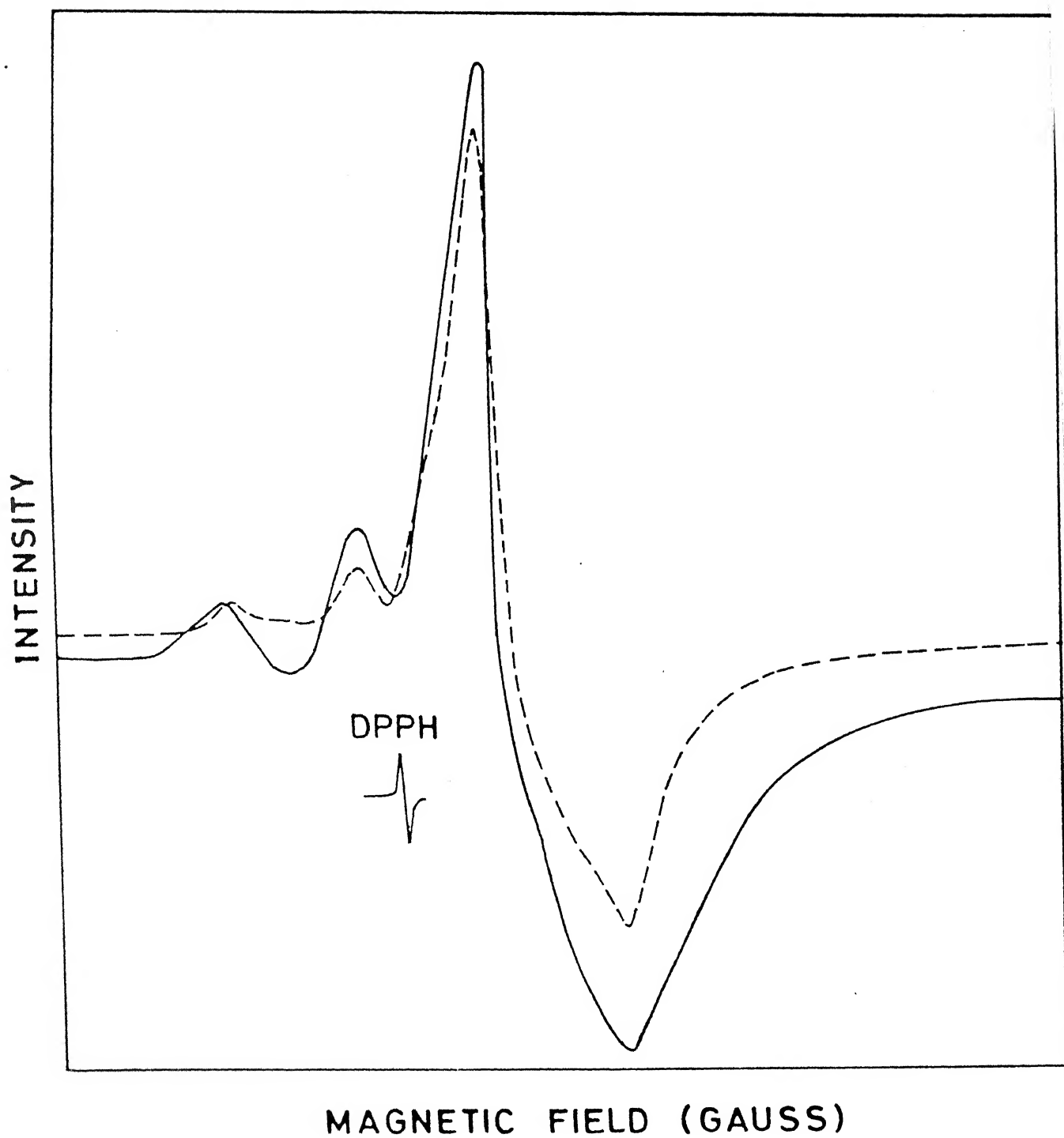
Fig.V.7   ESR spectra of polycrystalline $[Mo(N_3S_2)Cl_2(Py)_2]$ at 298 K.

(————————) Experimental (————————) Simulated.
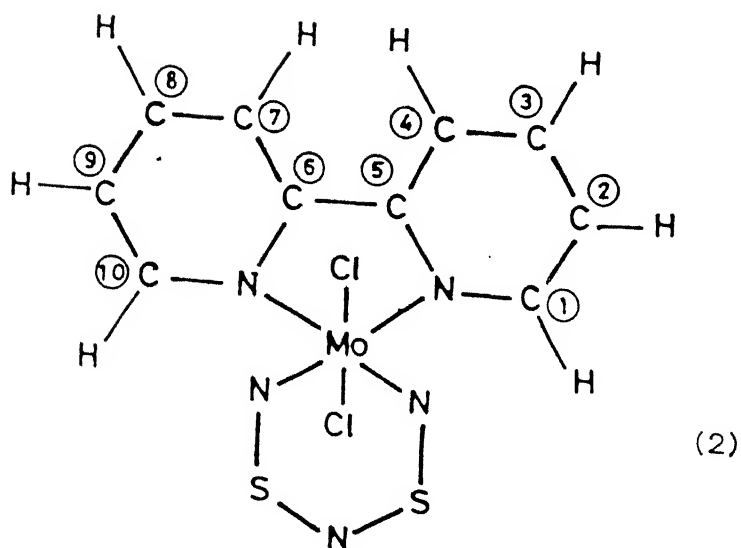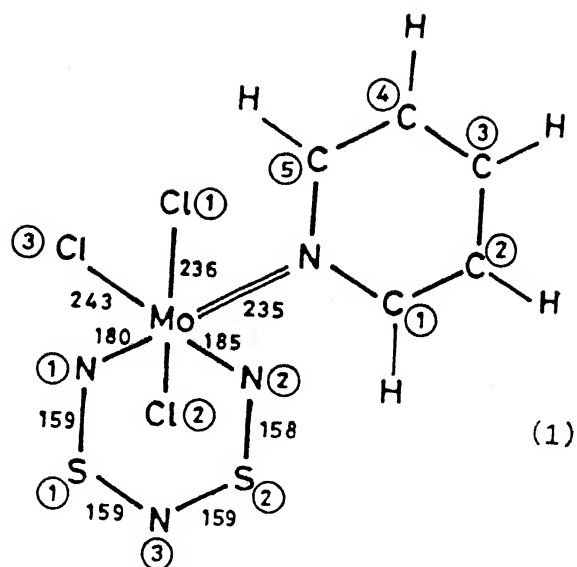
Fig.V.8 Structure of

(1) $[Mo(N_3S_2)Cl_2(Py)_2]$ from Ref.6

(2) $[Mo(N_3S_2)Cl_2bipy]$ – proposed.

Chapter — VI

Reactivity of Trithiazyltrichloride Towards
Arene Tricarbonyl Molybdenum(O) Complexes

The reactivity of trithiazyltrichloride with transition
metals and their compounds is an active area of research which is
well reflected in the synthesis and characterization of a reasonably
large number of metal complexes obtained as a result of such reacti-
ons. Despite the considerable growth, these reactions appear to be
unusual in the sense that the nature of S-N moiety coordinated to
the metal center is sensitive to the reaction conditions and varies
with slight change in any of the factors governing the reaction.
Besides, the mechanistic aspects of such reactions are in embryonic
state. It is, therefore, thought that further investigations in
this direction may be highly rewarding. In this context the reacti-
vity of trithiazyltrichloride with several η^6-arene tricarbonyl
molybdenum(O) complexes has been studied and the results are presen-
ted in this chapter.

VI.1 Experimental Section

All the chemicals used in these reactions are of chemically pure grade. The η^6-arene tricarbonyl molybdenum(0) complexes[1] (arene = benzene, toluene, xylene, anisole, mesitylene and hexa-methyl benzene), trithiazyltrichloride $(NSCl)_3$ [2] and $[Mo(N_3S_2)-Cl_3]_2$ [3] were prepared by the literature methods. The analytical procedures for characterization of the complexes IR(KBr), magnetic measurements and X-ray powder pattern were done by the methods described in earlier chapters.

Procedure

A typical reaction of $ArMo(CO)_3$ was carried out as follows: A saturated solution of $(NSCl)_3$ in dichloromethane (10 ml) was added dropwise with stirring to 10 ml solution of $ArMo(CO)_3$ (0.5 mmol) in dichloromethane whereby gas evolution occurred with the formation of brown precipitate. After the gas evolution had totally ceased, the precipitated brown compound was filtered, washed with dichloromethane and petroleum ether ($40°-60°C$). The product was dried in vacuo (yield, 95%). The same reaction was repeated with all the arene complexes at different temperature (upto $-78°C$). In every case the same complex was isolated which was identified as $[Mo(N_3S_2)Cl_3]_2$.[4] Found N, 13.2; Cl, 35.1; S, 19.9; Calculated for $[Mo(N_3S_2)Cl_3]_2$: N, 13.6; Cl, 34.8; S, 20.7; IR(KBr): 950(vs) $(\nu_{Mo=N})$, 340(vs) ν_{MCl}.

VI.2 Results and Discussion

The oxidative decarbonylation of various $ArMo(CO)_3$ by $(NSCl)_3$ proceeds with an immediate formation of $[Mo(N_3S_2)Cl_3]_2$ at wide range of temperature ($35°$ to $-78°C$). Analogous oxidations of arenetricarbonyl molybdenum(0) complexes using I_2 and $NOCl$ as oxidants have been reported earlier.[6,7] Relatively weaker oxidizing agents, such as I_2, lead to the formation of products having both arene and carbonyl groups bonded to the metal center while comparatively stronger oxidizing agents, such as $NOCl$, yield an intermediate $[Mo(CO)_2(NO)_2Cl_2]$ having no coordinated arene group but carbonyl groups.

Trithiazyltrichloride oxidations of arene tricarbonyl molybdenum(0) afford a product having neither arene nor carbonyl groups bonded to the metal. All efforts to isolate an intermediate similar to $[Mo(CO)_2(NO)_2Cl_2]$ even at lower temperatures failed which could possibly be due to high reactivity and high oxidizing power of $(NSCl)_3$ (vide supra). The latter was further substantiated by the observation that the substituted arenes with electron donating groups stabilize the $[Ar(CO)_3Mo]$ moiety, as reflected by the considerable differences in the rates of reactions between $NOCl$ and arene complexes.[8] Besides, inspite of relatively lower rates of reactions of $[ArMo(CO)_3]$ Ar = mesitylene or hexamethyl benzene compared to when Ar = benzene or toluene, the reactions of $(NSCl)_3$ with all the arene complexes were instantaneous unlike

the reaction pattern of I_2 and NOCl.[9] In these reactions, trithi

azyltrichloride thus exhibits three functions (i) providing N_3S_2

ligand coordinated to molybdenum, (ii) oxidation of metal to +6

oxidation state and (iii) chlorinating the metal ion. These

functions though are known in literature, but the factors that

are responsible for the differences in the behaviors of $(NSCl)_3$

with different metal ions or their complexes are still obscure.

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4. The identity of the complex has further been verified by comparing its properties (analyses, spectral data, magnetic moment and X-ray powder pattern) with the authenticated complex whose crystal structure has been determined by X-ray single crystal studies. Furthermore its reactions with THF, pyridine 2,2'-bipyridine and o-phenanthroline yielded $[Mo(N_3S_2)Cl_3THF]^3$, $[Mo(N_3S_2)Cl_3Py]^3$, $[Mo(N_3S_2)Cl_2 \ bipy]^5$ and $[Mo(N_3S_2)Cl_2o\text{-phen}]^5$ respectively.

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9. Though the reaction of η^6-(hexamethylbenzene) molybdenum tricarbonyl with trithiazyltrichloride was relatively slower compared to that of the benzene molybdenum complex, it was relatively too fast to isolate the intermediate product.

Chapter - VII

Summary and Scope for Future Work

The bidentate nitrogen aromatic heterocyclic ligands are one of the more favorite ligands of inorganic chemists in recer times. Interest in bi/polymetallic complexes having these bridg ing ligands arise from the fact that these complexes (generally photoinert) possess a highly absorbing MLCT transitions in the visible spectrum and undergo emission in solution. These proper ties make such complexes ideally suited for the study of bimole- cular water splitting or energy transfer processes.

Another area of profound interest is the study of chemist of sulfur-nitrogen compounds. Eversince the realization of the anisotropic properties associated with $(SN)_x$ polymers, the sulfu nitrogen chemistry has progressed enormously. Transition metal complexes with S-N species as ligands are important because they stabilize the unstable S-N species like $NSCl^{2-}$, S_2N_2, S_3N_2, etc through coordination and have the potential of forming low dimens onal polymeric complexes. Everthough numerous complexes of

transition metals having various coordinating S-N species are ?
ted and well characterized, there is still no reagent available
for the generalized synthesis of these complexes. Besides, no
effort has been made to understand the nature of bonding of the
metal ions in these species. It was therefore felt interesting
initiate some work in the areas because of the importance of th
polymetallic systems and the complexes with sulfur-nitrogen
compounds.

The syntheses and other detailed studies have been carrie
out on the bimetallic complexes of Group 6 carbonyls having α,α'
diimine as the bridging ligand. The ligands, p-phenylene bis-
(picolinaldimine) [PBP] and p-biphenylene bis(picolinaldimine)
[BBP] have been used as they have highly delocalized π-framework
similar to bipyridine and o-phenanthroline. The complexes of th
type $[M(CO)_4]_2$PBP/BBP were synthesized and characterized by IR,
UV-VIS and other related techniques. The reactivities of $[M(CO)$
PBP/BBP towards π-acid ligands L' $[L' = PPh_3, AsPh_3, SbPh_3, Py,$
Diphos] have been studied to examine the effect of the π-acidity
of the ligand L' on the properties of $[M(CO)_3L']_2$PBP/BBP, formed
after the reaction. ν_{CO} in the complexes has been assigned on
the basis of Cotton-Kraihanzel method. These complexes displayed
highly interesting electronic spectra. The MLCT band which exhi
ted negative solvatochromism has been shown to correlate with the
various solvent parameters and with the positions of the ν_{CC}. Th
effect of π-acidic properties of the coligand, L' is also reflecte

on the energies of the MLCT transition. Their electrochemical data indicated the possibility of two electron reduction of the ligands. The redox behaviors of $[Mo(CO)_4]_2PBP/BBP$ were also studied chemically. The fact that these complexes have MLCT band energy lower than the energy of the ligand field excited state (photoinert) and underwent emission in solution make such studies more interesting. These results have been compiled in the chapter II of the thesis.

The remaining chapters of the thesis describe the studies on syntheses, characterizations and nature of bonding in complexes of Group 6 metals having sulfur-nitrogen ligands.

Chapter III gives the synthesis of chlorothionitrene and cyclo disulfurdinitride complexes of Mo, W and Cr respectively. The chlorothionitrene complexes of Mo and W in +5 oxidation state were synthesized by the reactions of trithiazyltrichloride on $[M(CO)_4(L-L)]$ $[(L-L) = bipy, o-phen]$. The coordination mode of NSCl in the complexes was identified by the infrared spectral data and their chemical behaviors. The magnetic properties were studied using the results of magnetic susceptibility and ESR spectral data of these complexes. The magnetic susceptibility data suggested the reduced value of the 'orbital reduction factor, k' and thus suggesting the symmetry of these complexes lower than O_h. Besides characterization, the electronic spectra of the chromium complexes were analyzed in detail, from which the ligand field parameters, 10 Dq, β_{35} and β_{55} were calculated. On the basis of their values

$(\beta_{35}$ and $\beta_{55})$ (< 1), the relative contributions of $\sigma-$ and $\pi-$ characters in the metals ligand bonds have been derived.

Chapter IV is the extension of the chapter III where it was shown that the metal ions in M(II) complexes (M = Mo, W) get oxidized with trithiazyltrichloride to metal in +6 oxidation state during the reactions. They yielded chlorothionitrene complexes of the type $[M(NSCl)Cl_3X'(L-L)]$ from $[M(CO)_3X_2(L-L)]$ $[L-L = $ bipy, o-phen; $X_2 = Br_2$, I_2; $X' = Cl$, $Br]$. Thermolysis of the chlorothionitrene complexes yielded polymeric nitrido complexes. The same thionitrene complexes were also obtained by the reactions of bipy/o-phen with $[M(NSCl)Cl_4]_2$ whose crystal structure has already been published in the literature. The chemical and other spectroscopic results confirmed the presence of thionitrene group in the complexes.

Chapter V embodies the reactions of diimines (bipy and o-phen) and pyridine with $[Mo(N_3S_2)Cl_3]_2$ and $[Mo(N_3S_2)Cl_3]_2- \mu-S_2N_2$. Both the reactions yielded $[Mo(N_3S_2)Cl_2(Py)_2/bipy/o-phen]$ with Mo in +5 oxidation state. However, the yields of the products was much lower ($\sim 20\%$) when the former complex was used as starting material. In the latter case, the yield was found to be $\sim 80\%$. The enhanced yield in latter reactions has been attributed to the presence of S_2N_2 moiety. It was presumed that the extra electrons for the reduction of Mo from +6 to +5 oxidation state were provided by the S_2N_2 species containing π^* electrons. The latter itself got oxidized to uncharacterized S-N species which didnot coordinate

to the metal center. The ESR and the electronic spectra of the complexes were characteristic of the octahedral complexes with axial distortion. The same conclusion has been reached from the magnetic susceptibility data. The analyses of the molecular zeeman tensors (g and A, respectively) have been carried out by fitting computer simulated line shapes (Gaussian) to the experimental spectra. The anisotropic spectra was characteristic of $g\perp > g_\parallel$. From the shifts of the g values and using the electronic transition energies, the molecular orbital coefficients for the in-plane σ and π-bonding and out of plane π-bonding orbitals were evaluated These values indicated a high degree of covalency in the metal nitrogen bond of $N_3S_2^{3-}$ ring. It is also suggested that the electron is mostly present in the d_{xy} orbital and is only partially delocalized over the ligands in the equatorial plane.

Chapter VI gives the results of the oxidation reactions of the arene tricarbonyl molybdenum(O) complexes with trithiazyltrichloride, at room and low temperature ($-78^{o}C$). The results have been compared with those of the oxidation reactions of arene tricarbonyl molybdenum(O) using NOCl and I_2 as oxidizing agents under similar reaction conditions. The effect of the substituent groups on the arene ring, on the reaction rates has also been explored.

The work described in the thesis could further be extended in the following directions:

(i)   It has been indicated in the beginning of the chapter that
        the binuclear complexes have gained attention in the recent
        past because of their importance in energy transfer proce-
        sses, cooperative reactivity between the metal centers,
        electron transfer from one metal center to the other through
        the bridging ligand, photocatalyzed water splitting processes
        etc. As the ligands chosen in the present work have conjuga-
        ted π-bond system, they can make the electron transfer
        process facile through the conjugated double bonds. So a
        systematic study of the synthesis of $Ru^{II}-L-Ru^{II}$, $Ru^{III}-L-$
        Ru^{III} and $Ru^{II}-L-Ru^{III}$ could be planned.

(ii)   The characteristically small HOMO-LUMO gap found for the
        electron rich sulfur-nitrogen rings suggest photochemical
        activity. Although, there has been no major effort to
        study the photochemistry of these compounds, a study in
        this direction is warranted.

(iii)   Though a large number of complexes having S-N ligands are
        known but there has been no effort to understand the
        mechanistic details of these reactions. A kinetic study
        of these reactions is an open area for further work.

(iv)   A change in the emphasis towards an attempt to understand
        the unique properties of complexes having S-N ligands may
        possibly take the scientific achievements to the forefront
        of coordination chemistry.

(v)   The role of coordination complexes containing sulfur ligands in relations to bio-inorganic chemistry and heterogenous catalysis may provide an incentive to work in the latter areas.
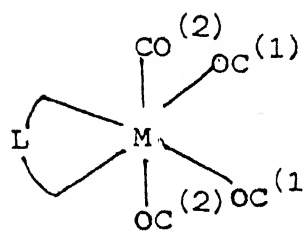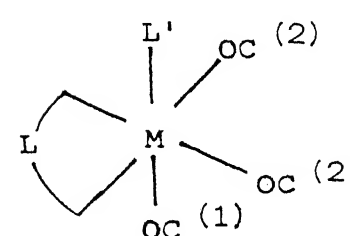
Besides, the problems described in the preceeding paragraphs, a few more areas in which one can work are the following:-

1. MO calculations of electronic structures of various coordinating S-N species.

2. The redox behavior of these electron rich systems.

3. Investigations of reactivity of the coordinated S-N species towards electrophiles, nucleophiles and unsaturated substrates.

4. The directed synthesis of transition metal S-N polymers with interesting solid state properties.

APPENDIX

Equations used for the calculations of various parameters.

A.I Cotton Kraihanzel method for the assignments of various carbonyl stretching modes.[1,2]*

Molecule	Molecular symmetry	Approximate Secular Equations

C_{2v}

$$\begin{array}{ll} A_1(1) \\ A_1(2) \end{array} \left| \begin{array}{cc} \mu(k_2+2k_i)-\lambda & 2\mu k_i \\ 2\mu k_i & \mu(k_1+k_i)-\lambda \end{array} \right| = 0$$

$$B_1 \quad \lambda = \mu(k_2-2k_i)$$

$$B_2 \quad \lambda = \mu(k_1-k_i)$$

C_s

$$\begin{array}{ll} A(1) \\ A(2) \end{array} \left| \begin{array}{cc} \mu k_1-\lambda & \sqrt{2}k_i\mu \\ \sqrt{2}k_i\mu & \mu(k_2+k_i)-\lambda \end{array} \right| = 0$$

$$B \quad \lambda = \mu(k_2-k_i)$$

---

* Force constants in dynes cm^{-1}. μ = reduced mass of the CO group, viz. $(16.00 + 12.01)/(16.00 \times 12.01) = 0.14583$; $\lambda = (5.8890 \times 10^{-2})\nu^2$, ν = frequency in cm^{-1}.

A.II Program for simulation of ESR Spectra

Computer program developed by Raghunathan and Sur[3] was used for fitting computer simulated line shapes to the experimental spectra.

A.IIIa Equations used for the evaluation of the molecular orbital coefficients, derived by DeArmond et al.[4]

$$g_{\parallel} - 2.0023 = -\left(2\frac{(2\lambda_M\beta_2\beta_1 - \lambda_L\beta_2'\beta_1')}{\Delta E(b_2^* \rightarrow b_1^*)}\right)(2\beta_2\beta_1 - 2\beta_1\beta_2'S_{b_2} - 2\beta_2\beta_1'S_{b_1} - \beta_1'\beta_2')$$

$$g_{\perp} - 2.0023 = -\left(\frac{2\lambda_M\beta_2\varepsilon}{\Delta E(b_2^* \rightarrow e^*)}\right)(\beta_2\varepsilon - \beta_2\varepsilon'S_e - \varepsilon\beta_2'S_{b_2})$$

$$-\frac{A}{P} = k\beta_2^2 + \frac{4}{7}\beta_2^2 + 2.0023 - g_{\parallel} + \frac{3}{7}(2.0023-g_{\perp}) - \frac{6}{7}\frac{\lambda_M\beta_2\varepsilon}{\Delta E(b_2^* \rightarrow e^*)}(\beta_2\varepsilon'S_e + \varepsilon\beta_2'S_{b_2})$$

$$+\left(2\frac{(2\lambda_M\beta_2\beta_1 - \lambda_L\beta_2'\beta_1')}{\Delta E(b_2^* \rightarrow b_1^*)}\right)(2\beta_2\beta_1'S_{b_1} + 2\beta_1\beta_2'S_{b_2} + \beta_1'\beta_2'),$$

$$-\frac{B}{P} = k\beta_2^2 - \frac{2}{7}\beta_2^2 + \frac{1}{1}\frac{1}{4}(2.0023-g_{\perp}) + \frac{11}{7}\left(\frac{\lambda_M\beta_2\varepsilon}{\Delta E(b_2^* \rightarrow e^*)}\right)(\beta_2\varepsilon'S_e + \varepsilon\beta_2'S_{b_2})$$

B Computer Programme for the calculation of β_1, β_2, ε.

```
        INTEGER M,N,IW(10),LIW,LW,IFAIL
        REAL X(3),FSUMSQ(4),W(100)
        EXTERNAL LSFUN1
        COMMON /VAL/ GPL,GPD,APL,APD,ZM,B1,B2,EPS,DEES,DEBS,DEB,P,RK,ZL
       1 ,BP1,BP2,SB1,SB2,SE,EPSP
C       BONDING PARAMETERS FROM THE EQUATIONS OF DeARMOND ET AL.,
C
        READ(20,*) GPL,GPD,APL,APD
        READ(20,*) P,RK,DEBS,DEES
        READ(20,*) ZM,ZL,SB1,SB2,SE
C
C
        N = 3
        M = 4
        LIW = 10
        LW = 100
        IFAIL = 1
        READ(20,*) X(1),X(2),X(3)
C
        CALL E04FDF(M,N,X,FSUMSQ,IW,LIW,W,LW,IFAIL)
        WRITE(5,501) IFAIL
        WRITE(5,502) X(1),X(2),X(3)
        STOP
501     FORMAT(5X,'IFAIL = ',I2)
502     FORMAT(5X,'SOLUTION : ',3F5.3)
        END
C
C
        SUBROUTINE LSFUN1(M,N,XC,FVECC)
        INTEGER M,N
        REAL XC(3),FVECC(4),D1,D2,D3
        COMMON /VAL/ GPL,GPD,APL,APD,ZM,B1,B2,EPS,DEES,DEBS,DEB,P,RK,ZL
       1 ,BP1,BP2,SB1,SB2,SE,EPSP
C
C
        B1 = XC(1)
        B2 = XC(2)
        EPS = XC(3)
        IF(B1.LT.0.0.OR.B2.LT.0.0.OR.EPS.LT.0.0) GO TO 50
        D1 = 1.0 - (1.0 - SB1**2) * B1**2
        D2 = 1.0 - (1.0 - SB2**2) * B2**2
        D3 = 1.0 - (1.0 - SE**2) * EPS**2
        IF(D1.GE.0.0.AND.D2.GE.0.0.AND.D3.GE.0.0) GO TO 100
50      FVECC(1) = 1.
        FVECC(2) = 1.
        FVECC(3) = 1.
        FVECC(4) = 1.
        GO TO 200
100     BP1 = (SB1*B1 + SQRT(D1))/1.0
        BP2 = (SB2*B2 + SQRT(D2))/1.0
        EPSP = (SE*EPS + SQRT(D3))/1.0
        WRITE(5,*) B1,B2,EPS
        FVECC(1) = GPL - 2.0023 + 2.*(2.*ZM*B1*B2-ZL*BP1*BP2)*
       1 (2.*B1*B2-2.*B1*BP2*SB2-2.*B2*BP1*SB1-BP1*BP2)/DEBS
        FVECC(2) = GPD - 2.0023 + 2.*ZM*B2*EPS*(B2*EPS-B2*EPSP*SE
       1 -EPS*BP2*SB2)/DEES
        FVECC(3) = APL/P + RK*B2**2 + 4.*B2**2/7. + 2.0023 - GPL
       1 + 3.*(2.0023-GPD)/7. + 6./7.*ZM*B2*EPS*(B2*EPSP*SE+EPS*BP2*
       2 SB2)/DEES + 2.*(2.*ZM*B1*B2-ZL*BP1*BP2)*(2.*B2*BP1*SB1+
       3 2.*B1*BP2*SB2+BP1*BP2)/DEBS
        FVECC(4) = APD/P + RK*B2**2 - 2./7.*B2**2 + 11./14.*(2.0023-
       1 GPD) + 11./7.*ZM*B2*EPS*(B2*EPSP*SE+EPS*BP2*SB2)/DEES
        WRITE(5,*) FVECC(1),FVECC(2),FVECC(3),FVECC(4)
C
200     RETURN
        END
```

A.IVa   Equations derived by Kon and Sharpless.[5]

$$(g_{||}/2.0023)-1 = -(1/E(b_2^* \to b_1^*))(2\beta_1\beta_2\lambda_M - \beta_1'\beta_2'\lambda_L) \times (2\beta_1\beta_2 - 2\beta_1'\beta_2') +$$

$$(1/E(b_1 \to b_2^*)) \times (2\beta_1'\beta_2\lambda_M + \beta_1\beta_2'\lambda_L)(2\beta_1'\beta_2 + \beta_1\beta_2')$$

$$(g_\perp/2.0023)-1 = -\left(\lambda_M\beta_2^2\varepsilon^2/E(b_2^* \to e^*)\right)$$

$$A/P = -\frac{4}{7}\beta_2^2 - k\beta_2' - 8\lambda_M\beta_2^2 \times \left(\frac{\beta_1^2}{E(b_2^* \to b_1^*)} - \frac{\beta_1'^2}{E(b_1 \to b_2^*)}\right) - \frac{6}{7}\frac{\lambda_M\beta_2^2\varepsilon^2}{E(b_2^* \to e^*)},$$

$$B/P = \frac{2}{7}\beta_2^2 - k\beta_2^2 - \frac{11}{7}\lambda_M\beta_2^2\varepsilon^2/E(b_2^* \to e^*).$$

A.IVb   Computer program to evaluate the parameters, $\beta_1, \beta_2, \varepsilon$.

```
      INTEGER M,N,IW(10),LIW,LW,IFAIL
      REAL X(3),FSUMSQ(4),W(100)
      EXTERNAL LSFUN1
      COMMON /VAL/ GPL,GPD,APL,APD,ZM,B1,B2,EPS,DEES,DEBS,DEB,P,RK,Z
     1 ,BP1,BP2,SB1,SB2,SE,EPSP
C
C
      READ(20,*) GPL,GPD,APL,APD
      READ(20,*) P,RK,DEBS,DEES,DEB
      READ(20,*) ZM,ZL,SB1,SB2,SE
C     CALCULATION OF BONDING PARAMETERS USING THE EQ. OF KON-SHARPLE
C
      N = 3
      M = 4
      LIW = 10
      LW = 100
      IFAIL = 1
      READ(20,*) X(1),X(2),X(3)
C
      CALL E04FDF(M,N,X,FSUMSQ,IW,LIW,W,LW,IFAIL)
      WRITE(5,501) IFAIL
      WRITE(5,502) X(1),X(2),X(3)
      STOP
501   FORMAT(5X,'IFAIL = ',I2)
502   FORMAT(5X,'SOLUTION : ',3F5.3)
      END
C
C
      SUBROUTINE LSFUN1(M,N,XC,FVECC)
      INTEGER M,N
      REAL XC(3),FVECC(4),D1,D2,D3
      COMMON /VAL/ GPL,GPD,APL,APD,ZM,B1,B2,EPS,DEES,DEBS,DEB,P,RK,ZL
     1 ,BP1,BP2,SB1,SB2,SE,EPSP
C
C
      B1 = XC(1)
      B2 = XC(2)
      EPS = XC(3)
      IF(B1.LT.0.0.OR.B2.LT.0.0.OR.EPS.LT.0.0) GO TO 50
      D1 = 1.0 - (1.0 - SB1**2) * B1**2
      D2 = 1.0 - (1.0 - SB2**2) * B2**2
      D3 = 1.0 - (1.0 - SE**2) * EPS**2
      IF(D1.GE.0.0.AND.D2.GE.0.0.AND.D3.GE.0.0) GO TO 100
50    FVECC(1) = 1.
      FVECC(2) = 1.
      FVECC(3) = 1.
      FVECC(4) = 1.
      GO TO 200
100   BP1 = (SB1*B1 + SQRT(D1))/1.0
      BP2 = (SB2*B2 + SQRT(D2))/1.0
      EPSP = (SE*EPS + SQRT(D3))/1.0
      WRITE(5,*) B1,B2,EPS
      FVECC(1) = GPL -( 2.0023 -( 2.*(2.*ZM*B1*B2-ZL*BP1*BP2)*
     1 (2.*B1*B2-2.*B1*BP2*SB2-2.*B2*BP1*SB1-2.*BP1*BP2)/DEBS
     1 +(2.*ZM*BP1*B2+ZL*B1*BP2)*(2*BP1*B2+B1*BP2)/DEB))
      FVECC(2) = GPD - 2.0023 +( 2.*ZM*B2*EPS*(B2*EPS-B2*EPSP*SE
     1 -EPS*BP2*SB2)/DEES
      FVECC(3) = APL/P + RK*B2**2 + 4.*B2**2/7. + 8.*ZM*B2**2
     1 *(B1**2/DEBS-BP1**2/DEB) +( 6./7.*ZM*B2**2*EPS**2)/DEES
      FVECC(4) = APD/P + RK*B2**2 - 2./7.*B2**2 + 11./14.*(2.0023-
C     FVECC(4)=APD/P+RK*B2**2-2.*B2**2/7.+(11./7.*(ZM*B2**2*EPS**2/
     1 DEES))
C     GPD) + 11./7.*ZM*B2*EPS*(B2*EPSP*SE+EPS*BP2*SB2)/DEES
C     WRITE(5,*) FVECC(1),FVECC(2),FVECC(3),FVECC(4)
C
200
```

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